



Nanolifecycle

A Lifecycle Assessment Study Of The Route And Extent Of Human Exposure Via Inhalation For Commercially Available Products And Applications Containing Carbon Nanotubes.

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NANOLIFECYCLE

A LIFECYCLE ASSESSMENT STUDY OF THE ROUTE AND EXTENT OF HUMAN EXPOSURE VIA INHALATION FOR COMMERCIALLY AVAILABLE PRODUCTS AND APPLICATIONS CONTAINING CARBON NANOTUBES

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1.0 Executive Summary

- 1) This study is aimed at analysing the likely route and extent of human exposure to carbon nanotubes (CNTs) via inhalation for a set of representative CNT-containing products in a lifecycle perspective.
- 2) The study has been conducted by the Safety of nanomaterial Interdisciplinary Research Centre (SnIRC), led for this study by the Food and Environment Research Agency, with participation of other Academic and Industrial Experts.
- 3) As part of the study, a review of all available CNT-containing products was carried out, and a representative subset of the products was identified for exposure analysis. The three CNT-containing products selected for the study included lithium-ion batteries, epoxy adhesive resins, and textiles.
- 4) The study assessed the suitability of current lifecycle assessment (LCA) protocols for assessing inhalation exposure from CNT and other nano-products. The relevance and adequacy of the relevant ISO protocols was assessed in relation to nanotechnology products (especially CNT-containing products), and any inadequacies have been highlighted.
- 5) The study also analysed the possibility of exposure to CNTs arising via inhalation during all stages of the life cycles of the selected study products.
- 6) The findings of the study indicate that:
 - 6a) LCA is not a tool for exposure assessment. On the contrary, exposure assessments can provide information to LCA that is relevant for impact assessment of CNT releases. LCA is, however, useful in identifying the stages in the lifecycle during which exposure may be relevant.
 - 6b) There is an almost complete lack of data to enable both a full-scale LCA, or a quantitative exposure assessment. Due to unavailability of the required data, a simplified LCA approach was adopted in this study, focusing on the potential inhalation exposure during the lifecycle of the selected CNT-containing products. Also, the exposure assessment was limited to qualitative analysis because of the lack of data necessary for a quantitative assessment.
- 7) Both LCA and exposure analysis have shown that the material synthesis stage (both for CNT materials, and CNT-containing products) is prone to giving rise to inhalation exposure to CNTs. However, the few studies carried out so far have generally shown that nanoparticle emissions during synthesis can be effectively controlled through appropriate engineering measures. Significant inhalation exposure to CNT material at this stage should be preventable provided such processes are carried out under appropriate emission control and waste management procedures. The main emphasis from the exposure point of view, therefore, needs to be on other stages/ processes in the lifecycle of products, where any sophisticated emission control measures are not likely to exist, e.g. post-production handling, transportation, accidental release, and use and disposal of the relevant materials and products.
- 8) A brief summary of different lifecycle stages of CNT-containing batteries, textiles, and epoxy adhesive resin is shown in Table 1. Using the currently available level of scientific evidence, those stages in the lifecycle of each study product have been highlighted where inhalation exposure to CNT is possible.

Table 1: Potential Inhalation Exposure to CNTs during the lifecycle of selected products

Level of Evidence	Batteries	Textiles	Epoxy resin
Deliberately aerosolised CNT, with potential for inhalation exposure - Evidence in the literature, specific to CNT			
Deliberately aerosolised CNT, with potential for inhalation exposure - Analogous evidence in the literature, not specific to CNT			
Deliberately aerosolised CNT, with potential for inhalation exposure – but no evidence able to be sourced		Manufacturing (Coating) Transport (Accidents, fire)	
Free CNT, with potential for inhalation exposure - Evidence in the literature, specific to CNT	Manufacturing (Precursor material preparation)	Manufacturing (Handling and mixing) Use (Accident – exposure to high temperature) Manufacturing (Accidents, fire) Transport (Accidents)	Manufacturing (Precursor preparation) Manufacturing (Polymer compounding)
Free CNT, with potential for inhalation exposure - Analogous evidence in the literature, not specific to CNT	Recycling (Processing)	Manufacturing (Weaving) Manufacturing (Finishing) Use (Wear & tear) Disposal (Shredding / milling / recycling) Disposal (Incineration - uncontrolled)	Recycling (Processing)
Free CNT, with potential for inhalation exposure - No evidence able to be sourced	Manufacturing (Equipment maintenance) Manufacturing (Accidents) Disposal (Incineration - controlled conditions) Disposal (Incineration - uncontrolled conditions)	Manufacturing (Accidents - spillages)	Manufacturing (Equipment maintenance) Manufacturing (Waste materials) Manufacturing (Accidents) Disposal (Incineration - uncontrolled conditions)
Matrix-bound CNT particulate, with potential for inhalation exposure - Evidence in the literature, specific to CNT			
Matrix-bound CNT particulate, with potential for inhalation exposure - Analogous evidence in		Manufacturing (Spinning) Manufacturing	

Level of Evidence	Batteries	Textiles	Epoxy resin
the literature, not specific to CNT		(Weaving) Disposal (Shredding / milling / recycling)	
Matrix-bound CNT particulate, with potential for inhalation exposure - No evidence able to be sourced	Manufacturing (Electrode manufacturing prior to battery sealing) Transport (Accidents) Use (Accidents)		Manufacturing (Resin curing) Transport (Accidents) Use (Machining manufactured product) Use (Accidents) Disposal (Incineration)
Matrix-bound CNT, with minimal potential for inhalation exposure - Evidence in the literature, specific to CNT			
Matrix-bound CNT, with minimal potential for inhalation exposure - Analogous evidence in the literature, not specific to CNT		Use (Wearing)	
Matrix-bound CNT, with minimal potential for inhalation exposure - No evidence able to be sourced	Manufacturing (Battery assembly) Transport (Routine transport of manufactured batteries) Use (Routine use) Disposal (Waste collection) Disposal (Landfill)	Manufacturing (finishing, handling/ mixing) Transport (Finished items) Use (Washing) Use (Ironing) Disposal (Landfill) Disposal (Incineration)	Transport (Routine transport of materials) Use (Routine handling of liquid epoxy) Disposal (Waste collection) Disposal (Landfill)

9) In brief, the study has indicated that during post-production lifecycle stages:

- 9a) CNT-containing batteries are unlikely to pose a risk of inhalation exposure to the users, except in a situation where they are physically shattered or cut open. The likelihood of exposure also exists from accidental releases (e.g. fire), during manual recycling, and as a result of inappropriate disposal (e.g. incomplete incineration, or landfilling). People who may be at risk of exposure to airborne CNTs will be those working at the recycling facilities (especially manual recycling in developing countries), waste disposal premises, or in the immediate vicinity.
- 9b) CNT-containing epoxy adhesive resins will only carry a risk of inhalation exposure during use if there were conditions that could lead to formation of aerosols. The likelihood of exposure could also result from disposal through incomplete incineration of CNTs. It is also of note that epoxy resins generally have a relatively short shelf life (less than one year for a typical product). The large-scale use of such resins in the future would need appropriate mechanisms for safe disposal of the unused (unhardened, liquid) epoxy resin.

- 9c) Textiles, to which CNT was added on the outer surface of the yarn in a post-production coating process, were identified as the most likely product that can pose a potential exposure to airborne CNTs. Among the products and processes studied, this is the only case where a significant consumer exposure during use stage seems plausible. Other lifecycle stages of the CNT-coated textiles that may pose a likelihood of inhalation exposure, include recycling (shredding and milling of worn-out textiles), and disposal through incomplete incineration. People who may be at risk of exposure to CNTs in these scenarios will be those working at the recycling or waste disposal premises, or in the immediate vicinity.
- 10) Common to the three product types studied is the need for mechanisms for appropriate end-of-life treatments, e.g. separate collection of (spent) CNT-containing batteries, recycling of CNT-containing batteries and textiles under controlled conditions, and appropriate disposal methods that ensure complete destruction of CNTs. It is known that CNTs breakdown completely when heated at 740°C under oxidative conditions. It is, therefore, imperative that if final disposal of CNT-containing products relies on incineration, it is carried out under appropriately controlled conditions to ensure complete destruction of CNTs.
- 11) Urgent research is needed to address the almost total lack of exposure data for CNT-containing consumer products, and the appropriateness of end-of-life treatments. The findings of this study will help manufacturers in developing safer products through a better design that is aimed at minimising the likelihood of exposure to CNTs (and/ or other nanomaterials) during post-production stages of the product lifecycle.

2.0 Background

The advent of nanotechnologies has unleashed enormous prospects for the development of new products and applications for a number of industrial and consumer sectors. Currently, over 800 nanotechnology-derived consumer products are listed in the inventory maintained by the Woodrow Wilson International Center for Scholars⁸. The use of engineered nanomaterials (ENMs) in consumer products has also raised certain concerns over safety of the ENM-containing products to human health and the environment. Of particular concern amongst these products are those that contain carbon nanotubes, nanowires or nanorods (collectively referred as CNTs). CNTs can be single- or multi-walled, and are a particular elongated tubular form of fullerenes (carbon bucky balls). CNTs have very high tensile strength and are considered to be far lighter but much stronger than steel, making them potentially the strongest, smallest fibre known. CNTs also exhibit high electrical conductivity, high surface area, distinct electronic properties, and potentially high molecular adsorption capacity. The currently available CNT-containing consumer products range from sporting items, such as tennis rackets and hockey sticks, to bicycle and aeroplane parts, and a variety of CNT-coated products.

The possibility that consumers may be exposed to CNTs through use or disposal of the CNT-containing products has raised particular concerns, because CNTs share some structural resemblance with asbestos fibres. There are a few reports, which indicate the potential of CNTs to cause harmful effects in living organisms. A recent pilot study at the University of Edinburgh by Professor Ken Donaldson's group has indicated that long multi-walled CNTs introduced into the abdominal cavity of mice can manifest asbestos-like pathogenic effects that include inflammation and formation of lesions (termed 'granulomas'). Whilst the study

⁸ www.nanotechproject.org/inventories/consumer/

suggests a potential link between inhalation exposure to long CNTs and mesothelioma, there is insufficient information to assess whether there would ever be realistic exposure in the workplace, during product use, or through environmental contamination to reach a threshold dose in the mesothelium. It is, therefore, important that potential exposure to CNTs is assessed in a lifecycle context before commercial use of CNTs (especially long CNTs) becomes widespread. In this context, the current study was funded by Defra to identify the likelihood and possible pathways of exposure via inhalation using a selection of commercially available CNT-containing products. The level of current knowledge gaps and uncertainties in regard to potential exposure meant that the study considered different scenarios covering the whole life cycle of the CNT-containing products - from R&D to manufacture, transportation, formulation, use, and recycling/ disposal.

The lifecycle analysis (LCA) is essentially an environmental tool, which is complementary to risk assessment. LCA aims to address the whole life cycle of a product or a service, e.g. a product containing CNTs. An LCA would therefore include all the stages from production of CNTs, through transport to a manufacturer (and any subsequent further transportation), manufacture of CNT-containing product(s), use of product(s), to final disposal of the product(s). The protocols established by the International Organization for Standardization (ISO) provide recommendations on how to define this life cycle and what to consider in the definition. The aim of this study is to use LCA to inform and complement risk assessment, by estimating the potential exposure to CNTs throughout the lifecycle of selected products. The conventional LCA, however, does not cover two issues so well - the occupational exposure and the consumer exposure. This is primarily due to difficulties in collecting the data and modelling the exposure. The ISO protocols do not specify or restrict what can or can not be included in an LCA. Therefore, this study also took into consideration the current LCA methodologies and their suitability, to include workplace and consumer exposure, and to identify if there is a need for any adjustment in the methodologies to make them more relevant to ENMs (such as CNTs).

This study has attempted to collate all available information in regard to possible inhalation exposure to CNTs throughout the lifecycle of the selected products. The overall aim was to adopt an LCA approach to identify the critical stages within the lifecycle of selected CNT products that may pose inhalation risk.

2.1 Study objectives

The overall aim of this study was to identify the potential pathways, and assess the likelihood and extent of human exposure via inhalation that might arise throughout the lifecycle of selected commercially available articles containing carbon nanotubes, nanowires or nanorods (collectively referred as CNTs).

To achieve this aim, the study first identified a set of relevant products through a review of the available CNT-containing products. The study then attempted to collate the relevant data for exposure analysis, and estimation of potential human inhalation exposure throughout the whole life cycle of the selected products. For this, the study adopted a life cycle assessment (LCA) approach. It is clear from the study that the existing methodologies (as defined by ISO protocols) for LCA have not been designed specifically for nanotechnology products, and that there is a scarcity of data required for LCA. The study, therefore, assessed the suitability of ISO protocols for applicability and adequacy to exposure assessment, identifying any major discrepancies in the protocols and making recommendations for possible adjustments, revisions, or adaptations to render them more relevant to the assessment of exposure to

nanoparticles that might arise from nanotechnology products. Another main focus of the study was to identify the critical stages within the lifecycle of selected CNT-products that are likely to give rise to any significant inhalation exposure to human. The main objectives of the study are as follows:

- To conduct a review and report on all products containing CNTs, which are currently commercially available or present in the UK, and recommend a representative subset of these for inhalation exposure analysis.
- To evaluate and report on the suitability of current LCA protocols for assessing inhalation exposure from CNT and other nano-products.
- To assess the possibility of exposure to CNTs arising via inhalation during all stages of the life cycles of the agreed selection of representative products.
- To report on further inhalation exposure assessment work which may need to be carried out, but which cannot currently be done due to any identified limitations in the ISO protocols.

3.0 Selection of CNT Products for Study

3.1 Commercial Scale Production of CNTs

According to the US-based BCC Research, the global market for CNTs was estimated at \$79.1m in 2007, predicted to reach \$807.3m by 2011. CNT-based composites make up the largest share (>80%) of the market⁹. Another report by Global Industry Analysts Inc. suggests the global CNT market is likely to exceed US\$1.9 Billion by 2010. According to the report, the CNT market is dominated by the US, whilst the EU is projected to be the fastest growing market for CNT products. Current forecasts also estimate that the global market for CNTs will grow by 25% per annum. In ten years, annual sales of these products are expected to reach US\$2 billion.

The major industrial manufacturers of CNTs include Bayer Material Science, who opened a new CNT production facility at Laufenburg on the German-Swiss border in 2007, doubling their production to 60 tonnes per year. They plan to open new plants to take production up to 300 tonne/year. Another major manufacturer Nanocyl (Belgium), have a production capacity of 40 tonnes a year.¹⁰ Other chemical companies are also boosting up their production of CNT. For example, the French chemical company Arkema has opened a CNT pilot plant in France in 2006 with an annual production capacity of 10 tonnes. In the UK, Thomas Swan & Co. Ltd. are the producers of single and multi-walled CNTs

In terms of R&D, the German Federal Ministry for Education and Research (BMBF) are supporting the InnoCNT that has more than 70 partners from industry and science aiming for development of new technologies and applications for CNT-based materials.

Large commercial-scale production of CNTs is understood to have already brought the price of CNTs to from around US\$200 per gram in 1999 to around US\$50 per gram.

3.2 Release Scenarios During Production of CNTs

There is a range of production methods for CNTs. However, the basic premise of all of them is to take a source of carbon, break it down typically to the atomic or diatomic levels and then reform the atoms into nanotubes. The needs of scalability and repeatability though, tend to mean that only three production routes have really been used for mass-production. These include:

- Catalytic chemical vapour deposition (CCVD) route - the dominant process used commercially.
- Arc-vapour route - only used by a few companies.
- Laser-oven route - no longer used for commercial scale production.

Both the laser and arc route can be considered as high temperature routes, where carbon is ablated at high temperatures (>2500 °C) by either a high power laser or electric arc. The ablated atoms then assemble into nanotubes. Under the right conditions, multi-walled carbon nanotubes (MWCNTs) can be produced from a pure carbon target or electrode. However, in order to produce single-walled nanotubes (SWCNTs) metal catalysts have to be introduced, by doping the target/ electrode. The CCVD route is a relatively low temperature process (200

⁹ www.nextbigfuture.com/2007/04/carbon-nanotube-market-projection-79.html - accessed 06 February 2009

¹⁰ Manufacturing the carbon nanotube market,
<http://content.stockpr.com/nanotailor/media/a0da718661c7255937283d166ca5687b.pdf>

to ~ 1300 °C) and uses a metallic catalyst to breakdown a (hydro)carbon feedstock (e.g. carbon monoxide, methane). It is generally accepted that smaller the catalyst particle, the smaller in diameter the nanotubes produced.

Table 1: Summary of the main CNT manufacturing routes and potential release scenarios during manufacturing stage

CNT manufacturing route	Possible CNT-release scenarios	Comments
<p>Catalytic Chemical Vapour Deposition (CCVD)</p> <p>The CCVD route has evolved from Baker's work on the catalytic production of carbon nanofibres. The route involves the cracking of a hydrocarbon catalyst over a metallic catalyst, from which the nanotubes then grow. Typically carbide forming catalysts such as iron, cobalt or nickel are used. However, the process has been shown to work with a wide range of metals, including gold. The catalysts may be made prior to the reaction or formed in-situ from precursors such as ferrocene during the nanotube growth process. The feedstock used is typically matched to the production temperatures involved, with more stable compounds (e.g. methane) being used at higher temperatures and less stable ones at lower temperatures (e.g. acetylene). The feedstock may also be diluted with inert gases (e.g. nitrogen and argon) or active gases such as hydrogen and ammonia. The size of the catalyst in general dictates the diameter of the nanotube, which grows from it. Hence for SWCNTs, < ~ 3nm catalyst particles are required, whilst 3 to ~ 50 nm particles are needed for DWCNTs. It is important to prevent the Oswald ripening of these catalysts at the high growth temperatures used. Hence the catalysts are either dispersed in the feedstock (<i>gas-phase production</i>) or held on a substrate (<i>substrate-bound production</i>).</p> <p>Gas-phase production has the obvious commercial advantage for bulk nanotube production that it has no substrate material to remove post-growth. Also, a continuous process is realisable by continually adding reactants at one of the reactor and collecting the nanotubes produced at the other. Gas-phase production, though, tends to make entangled agglomerates of nanotubes at the quantities required commercially. A well known example of a gas-phase production route is the HiPCO process developed in Rice University and scaled up by CNI in the USA. The manufacturing processes are catalysed by metal particles such as cobalt, nickel, iron etc, that may remain as contaminants in the final product.¹¹ Other impurities, such as</p>	<p>During manufacturing stage:</p> <p>The production process based on CCVD should not present any exposure to CNTs for the workforce during growth of CNTs, as the process uses controlled atmospheres in sealed reactors. However, during synthesis by a gas-phase process, CNTs are formed as aerosol inside the reactor, and any leakage may lead to release of CNT aerosol, especially if the system is operating under pressure.¹³ The HiPCO process produces SWCNT with greater concentrations of aerosol than other production methods, which may be due to the lower density of the HiPCO produced SWCNT.¹⁴ Compared to this, CNTs formed in a substrate bound process are unlikely to be directly released into the air.¹⁵</p> <p>During recovery of CNTs:</p> <p>The removal of CNTs from the reactors may pose a risk of exposure to airborne particulates, unless suitable control measures are in place. The recovery of CNTs after a gas-phase process takes place in bag-filters, which are reverse-pulsed and CNTs re-collected into a receptacle. If the filters are ineffective, the CNT may escape and pose a risk of exposure to the workers, especially if there is air recirculation at the workplace.¹³ In vapour- phase process, the recovery of CNTs is generally by mechanical means. This may also result in aerial escape of CNTs, but they are most likely to be in agglomerated bulk powder form rather than free CNTs.¹⁵</p>	<p>The CCVD route is the dominant process used to make CNTs commercially due to its relative ease of scalability.</p>

¹¹ Moisala A, Nasibulin AG, Kauppinen EI. The role of metal nanoparticles in the catalytic production of single-walled carbon nanotubes e a review. J Phys Condens Matter 2003;15: 3011-3035.

<p>amorphous carbon, nano-sized graphite structures and carbon encapsulated catalytic metal nanoparticles that may be present in substantial amounts (up to 40% by weight).¹²</p> <p>Substrate-bound bulk production involves the reaction of catalysts typically held on silica or magnesium oxide substrates in either a fixed bed or fluid bed configuration. The substrate is then removed using acids after growth.</p>	<p>During cleaning/ maintenance of reactor: Cleaning and maintenance of the reactor, and disposal of waste materials may also give rise to the release of CNTs.</p> <p>During post-production handling: Post-production handling of CNTs may include purification of fractions using a number of different such as solubilisation, filtration, centrifugation, and other separation techniques. CNTs may also be functionalised by linking different functional groups to the surface.¹⁶ The functionalisation of CNTs is likely to alter some of the physicochemical properties of CNTs – e.g. in terms of increased solubility, or ability to bind with other matrices.</p> <p>During transportation: Post-production transportation of CNTs is likely to be in sealed containers, and hence should pose no risk of exposure – except in the case of an accidental release.</p> <p>During formulation of products The processes involved in the formulation of CNTs into products will vary with the type of product, and are most likely to be carried out under necessary containment levels. The likely aerial emissions of CNTs may take place during transfer of (dry) materials from one receptacle to another. Cleaning of the formulation equipment may also release CNTs into wastewater.</p> <p>Disposal of industrial waste: It is not clear how industrial</p>	
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¹³ Aitken R, Creely KS, Tran CL. Nanoparticles: an occupational hygiene review. Edinburgh: Institute of Occupational Medicine; 2004.

¹⁴ Maynard AD, Baron PA, Foley M, Shvedova AA, Kisin ER, Castranova V. Exposure to carbon nanotube material: aerosol release during the handling of unrefined single-walled carbon nanotube material. J Toxicol Environ Health A 2004;67(1):87-108.

¹⁵ Kohler AR, Som C, Helland A, Gottschalk F. (2008) Studying the potential release of carbon nanotubes throughout the application life cycle, Journal of Cleaner Production 16: 927-937.

¹² Giles J. Growing nanotech trade hit by questions over quality. Nature 2004; 432:791.

¹⁶ Hirsch A, Vostrowsky O. Functionalization of carbon nanotubes. In: Schlüter AD, editor. Topics in current chemistry, 245. Berlin/Heidelberg: Springer; 2005. p. 193-237.

	waste is currently dealt with, i.e. whether it is recycled, incinerated, or land-filled.	
<p>Arc-vapour</p> <p>A typical apparatus set-up for the arc vapour method is shown in Figure 1. The electrodes are made from graphite with the anode 6-10 mm in diameter and the cathode twice the diameter of the anode. The distance between the electrodes is 1 to 3 mm. The chamber is usually filled with helium at a pressure of 500 to 600 Torr. (Helium is preferential to argon since it ionises more easily.) The arc is started by applying a current of 60 to 200A across the electrodes at a voltage of 25 to 50V. The plasma formed in-between the electrodes has a temperature of ~ 3700°C and the current density at the surface of the anode at 150A cm⁻². The high temperature sublimates the carbon and the anode is consumed. The anode is move as it evaporates to maintain a constant distance between the electrodes in order to sustain the arc. The MWNTs are found to deposit on the cathode and the walls of the chamber.</p> <p>SWNTs can be produced by drilling a hole in the anode and filling it with a mixture of graphite and approximately 0.1 to 6% of a metal. This method was announced in the same issue of Nature by two independent groups, Iijima <i>et al.</i> and Bethune <i>et al.</i> Since the publications, various catalysts and combinations of catalysts have successfully been used. These include Co, Fe, Ni, La, Y, Fe-Ni, Ni-Y, Rh, Pt, Rh-Pt, Ce-Ni, Co-S, Co-Bi, Co-Pb and Co-Pt. The SWCNTs are found to form web-like deposits throughout the chamber.</p>	<p>There is no obvious risk of exposure to CNTs to the operator during the running of the apparatus as the chamber is enclosed and run under a controlled atmosphere. This assumes adequate filters on the exhaust gas outlet. The possible risk of CNT exposure may occur during the breaking of the chamber's seals and harvesting of the nanotubes, depending on local extraction procedures and rules. It should be noted that majority of the CNTs produced in this route deposit as agglomerates rather than individual nanotubes, however information on airborne CNTs, if any, is currently not available.</p> <p>All further exposure possibilities throughout the CNTs' lifecycle are equivalent to that of the CCVD-produced CNTs described above.</p>	The arc-vapour route is only used by a few companies.
<p>Laser Oven</p> <p>A typical apparatus set-up for the laser oven method is shown in Figure 2. A pulsed Nd-YAG is scanned across the surface of the graphite target. The graphite vaporises and then is swept towards a water-cooled copper target where a carbonaceous deposit is found. This deposit contains 30% MWCNTs at the optimal oven temperature of 1200 °C. As the oven temperature is lowered the purity and quality of the nanotubes drop until 200 °C at which no nanotubes are formed. SWCNTs are produced using the same apparatus as for MWCNT production but substituting the graphite target for a mixed metal-graphite target. The typical target composition used is Ni_{0.6} Co_{0.6}C_{98.8} for which purities of SWCNTs of up to 90 vol% are obtainable. Variations on the production set up include using more lasers or switching to a continuous laser.</p>	<p>As with arc-vapour method, there should be no risk of exposure to CNTs to the operator during the growth process as long as suitable filters are in place on the exhaust. Similar concerns for collecting the CNTs after growth exist.</p> <p>All further exposure possibilities throughout the CNTs' lifecycle are equivalent to that of the CCVD-produced CNTs described above.</p>	The laser-oven route was used a lot initially to produce high quality SWCNTs but as far as we are aware it is no longer used for commercial scale production.

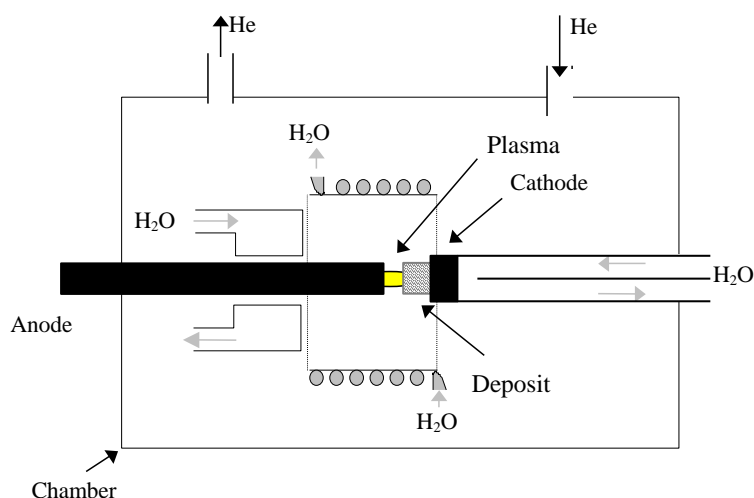


Figure 1: Example arc-vapour production apparatus

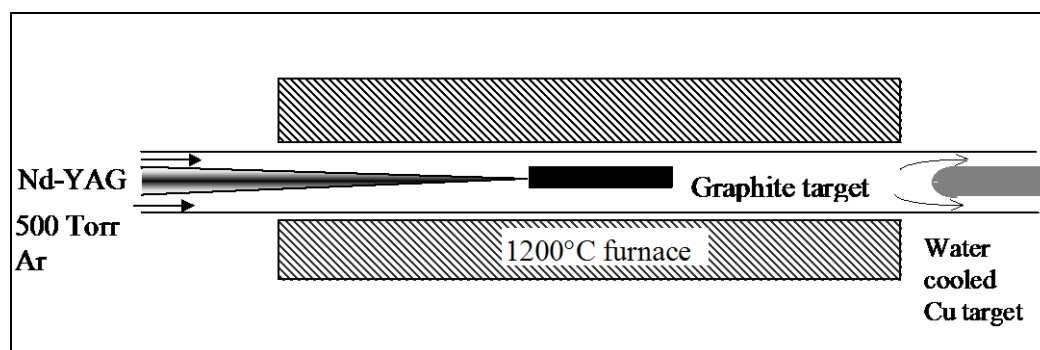


Figure 2: The apparatus used for the laser oven production route

3.3 Main Applications of CNTs

A list of the currently available CNT products is provided in Table 1. The following main areas of application have been identified from the search of published literature, company websites, product information, and inventories for CNT products.

Composites: Because of the high tensile strength, the main of use of CNTs is in structural materials, such as ceramic and polymer composites, and conducting composites for the aerospace, automotive and electronics industries, and adhesive such as epoxy resin (Table 1).

Electronic components: A large area of CNT application is likely to be in the electronics sector. Because of greater mechanical strength and heat-dissipation, CNTs are likely to be used in heat-transfer units in a variety of electronic devices, such a computers, display devices etc. Other uses vary from still under R&D (such as capacitors, flexible displays,

hydrogen storage devices, solar (photovoltaic) cells, (bio)sensors) to near market (such as flat panel displays). Another major area of potential large-scale application of CNTs is as a cathode material in lithium-ion secondary (rechargeable) batteries. It has been quoted by Kohler et al. (2008)¹⁵ that CNTs are widely used in mobile phone and laptop batteries. However, the article refers to a single (unsubstantiated) quote,¹⁷ that batteries used in around 60% of cell phones and notebook computers contained MWCNTs. However, all the published studies indicate the potential of CNTs for use in batteries as a superior material for storage of charge, and therefore if the application is already not widespread, it is likely to be in the future.

Textiles: There are known military uses of CNT containing textiles as bullet-proof, lightweight vests. Other textiles are being developed in which CNTs can either be spun, coated on surface, or dispersed in the polymer matrix. Because of the high cost of CNTs, these areas of application have so far not seen a widespread use of CNTs, but future low-cost manufacturing may lead to large-scale applications in this area.

R&D: Currently a number of applications of CNTs are at R&D stage. These include sensing devices (e.g. chemical and pressure sensors, biosensors), biomedical applications (CNT based drug delivery vehicles), energy storage, industrial adhesives and other composite materials (such as for stronger packaging). Other potential applications have also been described, such as use in hair colouring and cosmetic compositions¹⁸, in which CNTs have been chemically functionalised or physically modified to increase their affinity for hair.

Table 2: CNT products currently available in the UK or elsewhere

Product/ Application	Company	Description	Available in the UK?
Epoxy resin	Zyvex www.zyvexpro.com/epovex.html	Epovex is a new line of liquid epoxy resins from Zyvex Performance Materials (ZPM). Epovex resins are high performance, carbon nanotube strengthened epoxies ideal for numerous composites and adhesives applications.	?
Bicycle frame	Bianchi www.bianchiusa.com/08_hoc_928_record.html	incorporates carbon nanotechnology (nanofibre ?). No further details available	?
Bicycle frame	BMC www.bmc-racing.com/en/us/bikes/technology/materials/	Incorporates CNTs. No further details available	?
Different bicycle parts (such as DeltaForce Carbon Bar)	Easton® Sports, Inc., Bicycle Products Group	Reinforced with CNTs	Yes
Baseball bat (Stealth CNT® Baseball Bat)	Easton® Sports, Inc.	Baseball bat reinforced with CNTs	?

¹⁷ www.aip.org/tip/INPHFA/vol-8/iss-6/p18.html - accessed 03 March 2009

¹⁸ Huang, Xueying, Kobos, Robert K. and Xu, Gann (2007) Hair coloring and cosmetic compositions comprising carbon nanotubes, US Patent 7276088

Tennis Racquet	Babolat®	Contain CNT incorporated to stiffen key areas of the racquet head and shaft	Yes
Giles G-200 Aircraft	Avalon Aviation	CNTs incorporated into airframe for increased strength and flexibility	No
Flat-screen display	Eikos Inc. www.eikos.com/dispplications.html	Flat-screen display incorporating CNT technology	?
Lone Star Spike shoes	Adidas	CNTs reinforced full-length shoe plate	?
Organic Light Emitting Diodes (OLEDs)	Motorola®	No details available	?
Nitro Hockey Sticks	Montreal Sports Oy	Hockey stick incorporating CNTs	Yes
Prototype Comp NT® Golf Club	Grafalloy®, Inc.	Improved strength of golf club with CNTs	Yes
TX Express Laptop Computer	LG® Electronics	CNTs technology used to reduce heat emissions	?
Evolution Golf Shaft	AccuFlex	Nano-composite (compared to high-density graphite) no more details available.	Yes

3.4 Selected Set of CNT-Products for Study

Based on the information, 3 applications types were identified to cover the versatile range of CNT products. One product from each area of application was selected for further study. These include:

Table 3: CNT-containing products selected for the current study

Application Types	Products selected for study	Notes
Products containing CNTs in bound or embedded forms – such as batteries and packaging materials.	Batteries (rechargeable, secondary batteries)	Potential use for laptops/ mobile phones and other mobile devices means that they are likely to be manufactured, used and disposed of at a large scale in the future.
Products containing CNT in a surface coating - such as textiles and flat-panel displays.	Textiles (made of CNT fibre, or coated with CNTs)	The reducing cost of CNTs is likely to lead to a boost in this area of application in the coming years.
Products containing CNTs in a (relatively) free form - such as a liquid epoxy resin.	Epoxy resin (due to improved performance)	Due to improved performance, products like these are likely to find wider and large-scale applications – e.g. in construction and DIY sectors.

3.4.1 CNT-containing Lithium-ion Batteries

The lithium-ion rechargeable batteries hold the charge by electrochemical intercalation of Li-ions in a graphite anode. The charge is released when lithium ions move from the anode to the cathode.¹⁹ This type of batteries is used in most mobile devices, such as mobile phones, laptop computers and other electronic devices. They are also reported to be used in power supply for hybrid electric vehicles.¹⁵ The use of SWCNTs in these batteries can enable storage of almost twice the energy density per mass unit than graphite.¹⁵ Because of the physical and chemical stability, large surface area, and greater electrical conductivity, SWCNTs can enable development of long-lasting and rapid-charging batteries (see¹⁵ and the references cited therein). It has been quoted by Kohler et al. (2008)¹⁵ that CNTs are widely used in mobile phone and laptop batteries. The article refers to a single (yet unsubstantiated) quote that batteries in about 60% of cell phones and notebook computers already contain MWCNTs²⁰. Nevertheless, a number of published studies indicate the potential of CNTs for use in batteries as a superior material for storage of charge, and therefore if the application is not widespread at present, it is likely to be in the future. The main limiting factor seems to be the current high cost of the CNT material.

Research into the use of CNTs in batteries includes use for both anode or cathode materials. For anode use, entangled CNTs have been incorporated in the form of a thin nonwoven mat (the so called- bucky paper²¹), as porous composite of CNT with superfine Ni-P/Si particles,²² or as composite with SnO comprising 90% CNT, 38% SnO, 5% carbon black, and 5% PTFE. For cathode application, the use of MWCNT has been suggested in the form of tubular cavity structure,²³ as nanocomposite of sulfur-containing MWCNT,²⁴ or as highly porous V₂O₅ aerogel with SWCNT.²⁵

CNT-containing Li-ion batteries (from Kohler et al. , 2008) ¹⁵	Possible CNT-release scenarios (from Kohler et al. , 2008) ¹⁵	Comments
Manufacturing process A typical cylindrical Li-ion cell consists of approximately 30 components, including solvents and electrolytes. Manufacturing process involves chemical and mechanical processing of the electrode materials. The cathode and anode are then separated by a polypropylene separator, wound around a plastic liner to form a cylindrical shape (termed a ‘‘jellyroll’’), which is placed in a steel can along with a plastic	Assuming a similar scheme is used for the manufacturing of CNT-containing batteries, CNT-release is possible during the manufacturing process until the cells are sealed. Some of the processes may include certain preparatory steps such as mechanical milling, mixing of materials, assembling and winding of the electrodes. Once batteries are assembled, there is less likelihood of CNT release. Some emissions may	Only minor possibility for emission of CNTs during preparatory stages of manufacturing (e.g. mechanical milling, mixing of materials) – most possible route of emission is through (improper) disposal of industrial wastes (e.g. rejected materials/ batteries). CNT released from Li-ion

¹⁹ Nishi Y. Lithium ion secondary batteries; past 10 years and the future. J Power Sources 2001;100:101-106.

²⁰ www.aip.org/tip/INPHFA/vol-8/iss-6/p18.html - accessed 03 March 2009.

²¹ Ng SH, Wang J, Guo ZP, Chen J, Wang GX, Liu HK. Single wall carbon nanotube paper as anode for lithium-ion battery. Electrochim Acta 2005;51:23-28

²² Shu J, Li H, Yang R, Shi Y, Huang X. Cage-like carbon nanotubes/Si composite as anode material for lithium ion batteries. Electrochem Commun 2006;8:51-54

²³ Q, Li H, Chen L, Huang X, Zhong D, Wang E. Investigation of lithium storage in bamboo-like CNTs by HRTEM. J Electrochem Soc 2003;150(9):A1281-1286.

²⁴ Zheng W, Liu YW, Hua XG, Zhang CF. Novel nanosized adsorbing sulfur composite cathode materials for the advanced secondary lithium batteries. Electrochim Acta 2006;51:1330-1335.

²⁵ Sakamoto JS, Dunn B. Vanadium oxide-carbon nanotube composite electrodes for use in secondary lithium batteries. J Electrochem Soc 2002;149(1):A26-30.

insulator. The can is filled with an electrolyte solution and covered with a well plate and cap. Manufacturing usually takes place under an inert gas atmosphere. After sealing, the cell is covered with a hard plastic wrap and is ready for use. ²⁶	be possible through the production waste materials.	batteries may have a porous wall structure and residues of intercalated lithium ions. ¹⁵
Use stage The Li-ion batteries are usually fitted as an integral part of electronic devices. Also, the CNT-material in batteries is sealed within a metal or plastic case, and hence the release of CNT materials is unlikely under conditions of normal use.	CNT release is possible if batteries are physically opened or are subjected to high temperatures. Some reports suggest a rare risk of fire hazard associated with Li-ion batteries. ²⁷ However, such a risk has been considered negligible in relation to the use of CNTs, as the vast majority of Li-ion batteries remain intact during the use phase. ¹⁵	Direct human exposure to the content of the batteries is unlikely during the use phase (only in rare cases of an incidental disintegration of the battery casing).
Handling, transportation	As above, CNT release is only possible if batteries are physically opened.	Direct human exposure to CNTs is unlikely except in an incidental disintegration of battery casing.
Recycling and disposal Li-ion batteries are most likely to be disposed of as electronic waste, with a smaller proportion through the normal waste streams. In some countries spent batteries are collected and recycled as a separate stream. In the EU (and Switzerland) waste regulations ^{15,28} require recycling prior to disposal. For recycling, the waste batteries are separately collected, or separated from other waste items. The CNT emission from CNT-containing batteries may take place during recycling as it will involve opening of the	As recycling is intended to recover metals (e.g. Fe and Co), the batteries are physically opened by mechanical shredding and/or milling, followed by mechanical sorting (such as by sieving or application of magnetic field), and thermal processing (such as pyrolysis and smelting). These processes may generate particulate emissions with likely release of airborne CNTs. Such releases are likely to be through the exhaust emissions of the recycling facilities if improper filters are used. There may be much greater likelihood of inhalation exposure in some parts of	Emissions of CNTs likely during recycling – e.g. mechanical recovery of metals. Direct exposure of workers is likely during manual recycling (in some countries). Non-recycled batteries (only a minor proportion) may be incinerated or landfilled. Both processes may not destroy CNTs completely and some environmental release is possible in the longer term.

²⁶ NEC TOKIN Corporation. Manufacturing process for prismatic type lithium ion rechargeable batteries, <<http://www.nec-tokin.com/english/product/me/chisiki/li6.html>>; 2006.

²⁷ http://technology.timesonline.co.uk/tol/news/tech_and_web/article4572316.ece, accessed 28 June 2009.

²⁸ In the EU, the substances that can be used in the manufacture of electrical and electronic equipment are regulated by Directive 2002/95/EC on the restriction of the use of certain hazardous substances in electrical and electronic equipment (RoHS Directive) and the manufacturing processes are covered by general environmental controls. Specific waste legislation in the form of Directive 2002/96/EC on waste electrical and electronic equipment (WEEE) governs the recovery and disposal of electrical equipment. This Directive also influences the design of the equipment to encourage recovery and recycling whilst requiring the establishment of waste collection systems and the setting of recovery and recycling targets. As a minimum, a number of specified substances, preparations and components have to be removed from any separately collected WEEE (waste electrical and electronic equipment) and treated as specified in the Directive: The list includes batteries. In addition, the Directive 91/157/EEC on batteries and accumulators containing certain dangerous substances (as amended) prohibits the placing on the market of certain batteries and accumulators containing lead, mercury or cadmium. It also promotes a high level of collection and recycling of waste batteries and accumulators and improved environmental performance of all operators involved in the lifecycle of batteries and accumulators, e.g. producers, distributors and end-users and, in particular, those operators directly involved in the treatment and recycling of waste batteries and accumulators. The Directive is implemented in the UK by the Batteries and Accumulators (Containing Dangerous Substances) Regulations 1994 (as amended).

<p>metal/plastic casing. However, this is likely to happen at the recycling facilities, not at the collection points. Kohler et al. (2008)¹⁵ have identified the following processing routes:</p> <ul style="list-style-type: none"> - automated sorting and dismantling of batteries, followed by recycling under controlled mechanical or thermal processing conditions (e.g. pyrolysis, smelting) - mechanical co-processing together with e-waste - manual sorting and dismantling by a workforce, based on improvised technology (e.g. open burning). 	<p>the world where battery recycling is carried out manually.</p> <p>Thermal processing of batteries also may not completely destroy CNTs; as they are reported to be transferred into granulate interstage products (e.g. cobalt fraction).¹⁵ These granulate materials have been considered a major source of CNT-emission because their handling would take place outside controlled environments.¹⁵</p> <p>A proportion of batteries may not be recycled, and instead be dumped into the normal waste streams. Such wastes are likely to end up as waste for incineration (or open burning in some developing countries), landfilling; illegal dumping. However, less than 0.04% of all batteries sold in Switzerland were missed out of recycling or incineration (reference 65 in ¹⁵).</p> <p>Free SWCNT burn out at around 600 °C in the presence of oxygen. Incineration temperatures are typically >850°C, and retention times of up to 60 minutes. These conditions are likely to destroy CNT materials. However, some densely packed CNT inside the metallic casing may not be exposed to oxygen during incineration.¹⁵ Under reductive conditions, SWCNT may reform into MWCNT at around 2200 °C. Therefore cylindrical cells, which enter the slag, can still contain some CNTs.¹⁵</p> <p>Batteries disposed off through landfilling are also likely to corrode over time. It is not known whether CNTs will migrate into soil/ water environments.</p> <p>CNT-containing batteries wrongly disposed of may corrode into the environment over time and release CNTs.</p>	
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3.4.2 CNT-containing Textiles

Despite a wide range of potential applications in the textile sector, the relatively high cost of CNTs has so far prevented large-scale use of CNTs in this area. However, a number of applications are at different stages of R&D. Different spinning processes can be used to make CNT fibres and yarns from agglomerated CNTs, or CNT fibres can be interwoven with other polymer yarns. In addition, there may be other possible applications of CNTs; for example:

- Where synthetic fibres have been surface coated with a layer of CNT;
- Where fabrics have been printed on with a CNT-containing material;
- Where CNTs are integrated into other polymers, through in situ polymerisation or dispersal in molten polymers, to produce composite master batches. Because of the aggregation of CNTs, their uniform dispersion in polymer matrices is generally problematic, and requires chemical modification of the CNT surface.

The short-term applications for textiles are expected to be mainly in the form of composites of CNTs with other polymers to improve mechanical or functional properties. It is also expected that first products incorporating CNT materials would be for the high-value sports wear, due to the current high cost of CNTs.

CNT-containing textile (from Kohler et al. , 2008) ¹⁵	Possible CNT-release scenarios (from Kohler et al. , 2008) ¹⁵	Comments
<p>Production stage:</p> <p>The production of CNT-containing textiles will involve production of materials such as polymers and master batches, and products such as fibres, yarns, fabrics and finished products (e.g. apparel).</p> <p>Material manufacture will involve processes such as melting, mixing, co-extruding, granulating.</p> <p>Product manufacture will involve fibre production - melting, spinning, weaving, sizing, knitting, bleaching, dyeing, printing, washing, drying/fixing, cutting, sewing, shaping, washing.</p>	<p>CNT-release is potentially possible in the early steps where the polymers are blended with CNTs to make master batches.</p> <p>Several methods can be used to disperse CNT in a polymer, e.g. the dry powder mixing method, liquid phase dispersion by ultrasonic treatment, in situ polymerisation, or using a twin-screw extruder. Some emission of CNT may be possible during such processes.</p> <p>Considerable particle release during spinning and weaving is not expected but fabric finishing and tailoring could potentially result in wet or dry abrasion of fibre fragments that may contain CNTs.¹⁵</p>	<p>Some information is available on the polymer CNT composite material compositions, the uses of which may include textiles. For example:</p> <p>Polyacrylonitrile /SWCNT fibres containing up to 10% SWCNT exhibit a 100% increase in tensile modulus at room temperature.²⁹</p> <p>Polypropylene/SWCNT composite fibres with 1% SWCNT, improved the tensile modulus of the fibres by 3 times.</p> <p>Up to 20% CNTs in polyethylene composites and 0.7% in Polystyrene composites have been developed.³⁰</p> <p>CNT from textiles may be surface functionalised or polymer coated.</p>
<p>Use stage:</p> <p>During use of CNT-textiles, degradation of the matrix could lead to release of CNT (because CNTs will be much more stable and will</p>	<p>During their life cycle, garments typically suffer a 10% weight loss.¹⁵ CNT-containing textiles are likely to be less prone to wear and tear; but some fibre fragments are</p>	<p>Garments are worn close to the human body over longer periods of time. If there was a release of CNT from textile fibres, some risk of direct dermal exposure</p>

²⁹ Sreekumar TV, Liu T, Min BG, Guo H, Kumar S, Hauge RH, et al. Polyacrylonitrile single-walled carbon nanotube composite fibers. *Adv Mater* 2004;16(1):58-61.

³⁰ Haggemuller R, Zhou W, Fischer JE, Winey KI. Production and characterization of polymer nanocomposites with highly aligned single-walled carbon nanotubes. *J Nanosci Nanotechnol* 2003; 3: 105-110.

<p>not degrade as polymers).</p> <p>Degradation of polymers can also happen due to UV-radiation, exposure to chemicals, water, or due to oxidation of polymer molecules.</p> <p>During use stage, the textiles are likely to undergo washing, ironing, exposure to sunlight, heat, sweat, microbial activity, as well as physical wear and tear.</p>	<p>likely to come off during use, which are likely to end up in wastewaters during washing, or in the environment as fluff or dust.</p> <p>Textiles may be exposed to heat during use (e.g. ironing, drying cycle). The effect of (UV) light on in the respect is not known. The physicochemical nature of the CNTs coming off the textiles is not known. It is of note that CNTs used in textile applications may not be of a uniform composition in terms of purity, length, degree of aggregation, wall structure and surface functionalisation etc.</p>	<p>would be likely, which may cause skin irritation.¹⁵</p>
<p>Recycling stage:</p> <p>Textile waste from industry is reclaimed and reused. Used clothes are collected by charities and resold in second hand shops or sent to developing countries.</p> <p>The destination of used consumer textiles in the UK has been mapped by Kohler et al (2008)¹⁵. The material may be shredded and fibres undergo screening and cleaning. They may be blended with other fibres for spinning. To recover some of the polymers, such as polyester, the textiles may be cut into pieces and granulated into small pellets. The pellets undergo processing to recover the polymer monomers that are re-polymerised and processed by extruding, melting, spinning etc into new fibre.</p>		<p>The recycling processes involve a variety of mechanical, thermal and chemical treatment processes. These processes may release CNT from composite fibres. The introduction of CNT-containing textiles into recycling may also cross contaminate other materials, especially if the materials are processed to recover polymer materials for re-polymerisation.</p>
<p>Disposal:</p> <p>In the UK at least 75% of fashion textiles are not recycled but landfilled at the end of their useful life.³¹ In Switzerland annually 5.5 kg textiles per inhabitant are disposed of and burned in municipal waste incinerators as a part of municipal solid waste.¹⁵</p>	<p>MWCNT and SWCNT have been shown to be burnt off completely at 740 °C under oxidative conditions. It is, therefore, likely that CNT/polymer composites would incinerate completely, and any remaining CNTs agglomerate with other particles in the waste gas stream and removed by the filter.</p> <p>Incineration in open fires (in developing countries) does not necessarily destroy the CNTs. As a consequence CNTs may enter the fume or the ashes and pose a risk of inhalation exposure.</p>	<p>The risk of human exposure to CNTs is likely to increase during recycling and disposal (especially at the vicinity) if the products decompose without destroying the CNTs (e.g. by shredding or low-temperature incineration).</p>

³¹ Waste Watch. Textile recycling information sheet, <<http://www.wasteonline.org.uk>>; 2006.

3.4.2 CNT-containing Epoxy Resin

The 3rd case study selected for this project is an epoxy resin containing CNTs. Because of greatly improved performance of adhesives and other materials made of such polymer composites, they are likely to find wider and large-scale applications in many sectors. A typical example of CNT-containing epoxy resin is the Zyvex's NanoSolve[®] Additive, which is available as a low viscosity liquid resin that can be hardened on mixing with a suitable initiator. The range of Zyvex products comprise the epoxy concentrate blends with MWCNTs, SWCNTs, or carbon nanofibers, and exploit the exceptional properties of the carbon nanomaterials in terms of tensile strength and electrical conductivity.³² The inclusion of CNTs in epoxy polymers is reported to greatly enhance the electrical, mechanical, and thermal performance compared to conventional fillers (e.g. carbon black, or other ultra-fine metal powders). However incorporating CNTs into polymers requires functionalisation of the CNTs external walls to overcome certain problems, such as in relation to phase separation, aggregation, and poor dispersion and adhesion. For the Zyvex products, such problems have been overcome through development of multi-functional CNT walls that non-covalently bind to the polymer matrices. One such functionalisation is based on cyclodextrin.³³ The company has developed the concentrates with different concentrations of CNTs (between 1 to 20 wt %) for different applications. The main application areas include glass, aramid, adhesives, coatings etc. The main sectors that could use the concentrates include sporting goods, defence, electronics and electronic packaging, rapid prototyping, aerospace components, and marine.

CNT-containing epoxy resin	Possible CNT-release scenarios	Comments
<p>Production stage:</p> <p>For the CNT-containing epoxy resin, the polymer resins, curing agents, and CNTs are manufactured by different manufacturers (MWCNTs by Arkema, and SWCNTs by Thomas Swan & Company).</p> <p>The concentrates use different epoxy resins – such Bis-phenol A, Bis-phenol F, Cycloaliphatic resins, or Tetraglycidyl methylene dianilines (TGDDM).</p> <p>The description of concentrates states that they are black viscous resin with a slight odour, with negligible solubility in water, and boiling point >200 °C. The composition of the concentrates states that they are bisphenol-F, CNT-strengthened, liquid epoxy resin suitable for numerous</p>	<p>DuPont have investigated the use of CNTs as nano-fillers to improve mechanical and electrical properties of engineering thermoplastics. The Dupont lifecycle assessment has highlighted the lack of information on physicochemical properties, health and environmental behaviour, fate and effect data. According to the study, CNTs are generally supplied as a black powder in the form of highly agglomerated visible fibrils with less dusting potential than carbon black, or as pellets, which are CNT concentrates encapsulated in a polymer. The following processes are generally involved:</p> <ul style="list-style-type: none"> - CNT powder compounded into a polymer melt using conventional batch mixers or continuous extrusion equipment. Incorporation may be by direct addition of the CNT powder into the compounder 	<p>The potential inhalation under polymer-CNT nanocomposite manufacturing, or use, is possible under conditions where exposure to powder dust, vapours or mists is possible.</p> <p>DuPont conducted area and employee exposure monitoring in a batch melt compounding operation using small quantities of representative MWNT's. The air monitoring results are described in Attachment 1. The results show that the samples were below the established OSHA permissible exposure level (PEL) guidelines for Total Dust (PEL 15mg/m³ for 8 hour TWA) and Respirable</p>

³² Yu, S., Tong, M.N., Critchlow, G. (2009) Wedge test of carbon-nanotube-reinforced epoxy adhesive joints, *Journal of Applied Polymer Science*, 111(6): 2957–2962.

³³ Chen, Jian, Dyer, Mark J. (2008) System and method for manipulating nanotubes, United States Patent 7344691, Zyvek Performance Materials, LLC, Columbus, OH, USA.

composites and adhesives applications. The company produces three types of concentrates: <ul style="list-style-type: none"> - Epovex ZS-250: vapour pressure 82 Pa at 20 °C, viscosity @25°C = 5,000-6,000 cPs - Epovex ZS-350: vapour pressure = 0.03 mbar at 77°C, viscosity @25°C = 8,000-9,500 cPs) - Epovex ZS-450: = viscosity @25°C = 22,000-24,000 cPs, Vapour pressure = 0.03 mbar at 77°C 	at the final composition (typically 0.5 to 5% by weight), or at high concentrations (5% - 50% by weight) to create a masterbatch. The composite product would normally be in a pellet form. <ul style="list-style-type: none"> - Addition of a pre-compounded CNT masterbatch pellet form into a melt compounding or shaping/forming process, commonly called a letdown step. - Addition of CNT powders into monomers, solvents or other carrier liquids for addition to polymerisation, compounding or shaping/forming processes. - CNTs are generally in powder form, with 0% to 4% impurities. - Masterbatch concentrations of CNTs may range from 5 – 50 wt.%, with 10-25% being typical. - Nanocomposite products may contain 0.1 – 10 wt.% CNTs, with 1–5% being typical. - The diameters range from ~0.4 to 	Dust (PEL 5mg/m3 for 8 hour TWA). ³⁴
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³⁴ Air monitoring was conducted by Dupont to evaluate potential exposure to CNTs while performing extrusion and molding of a mixture of an example polymer and a CNT. DuPont Industrial Hygiene experts sampled the workplace air to determine if exposure potential is being adequately controlled. Area samples were collected from various positions in the room around a sample preparation enclosure and small-scale batch mixing and injection molding systems. An air sampling device was worn by the research technician performing the nanocomposite synthesis experiments. Air monitoring and sample analysis was conducted in accordance with NIOSH method 0500 for Total Dust.

Some dust generation was observed, contained within ventilated enclosures, during operations involving handling of the powder. A condensation particle counter was used to measure concentrations of particles, in the range of 20 to 1000 nanometers, emitted from processes in close proximity to the point where material was handled during sample preparation (decanting CNTs from a jar or bag and weighing) and insertion into the mixing equipment. Particle count readings quickly rose when material was added and quickly fell to background levels, indicating that engineering controls were effectively collecting airborne particulate matter. Particle count readings were taken at the HEPA vacuum cleaner filter exhaust (filtered air). Levels dropped to below background levels, indicating that HEPA filter was removing airborne particles.

The results showed that the samples were below the established OSHA permissible exposure guidelines (PEL) for Total Dust, PEL 15mg/m3 for 8 hour TWA, and Respirable Dust, PEL 5 mg/m3 for 8 hour TWA. Currently, exposure limits have not been established for carbon nanotubes. Also, there are no established exposure guidelines for particles in the nano-sized range (less than 100 nm or 0.1 µm). Since an arbitrary PEL could not be set for CNTs, the engineering controls developed, PPE used and operating procedures adopted were designed to reduce exposure to as low a level as reasonably achievable. The air monitoring tests showed that exposure potential near the equipment ranged between the non-detection limit of the measurement and a maximum of 0.65 mg/m3.

Similar programs with other nanomaterials (e.g., TiO₂, SiO₂, nanoclays) have included monitoring of the workplace air during continuous melt compounding and post processing operations (grinding and cutting). The grinding and cutting tests of such composites have not thus far indicated any detectable regeneration of any nanoparticles.

[Dupont Nanomaterial Risk Assessment Worksheet: Incorporation of Single and Multi Walled Carbon Nano Tubes (CNTs) into Polymer Nanocomposites by Melt Processing, www.edf.org/documents/6553_CNTs_Summary.pdf]

	> 3 nm for SWCNTs, and from ~1.4 to at least 100 nm for MWCNTs. The length of CNTs varies from 100nm to several millimetres.	
Use stage: The concentrates are stated to be stable at room temperature, but can react vigorously with strong oxidising agents, strong lewis or mineral acids, and strong mineral and organic bases, especially primary and secondary aliphatic amines. Run-away cure reactions may char and decompose the resin system, generating unidentified fumes and vapours that may be toxic.		The company literature suggests that no respiratory protection would usually be required under normal conditions of use, and the use should be carried out in a well-ventilated area, skin contact should be avoided, and hands must be protected with butyl or EVAL-laminate gloves when handling. Lab coats and chemical goggles must be worn, as well as a face shield if molten product is used and there is a splash potential.
Recycling stage:	Not applicable	
Disposal: It is not clear how industrial waste is currently dealt with, i.e. whether it is recycled, incinerated, or land-filled.	The quoted shelf life for the study product is 9 months.	The short shelf-life of the product will need appropriate mechanism for the disposal of unused (unhardened, liquid) epoxy resin, potentially spread out within the wide supply chain.

4.0 Lifecycle Assessment (LCA)

The LCA methodology for a wide range of products and applications has been standardised in the two protocols - 14040 (2006) and 14044 (2006) - established by the International Organization for Standardisation (ISO).

The protocol 14040 sets out the principles and framework for performing LCA, whereas the protocol 14044 provides the necessary requirements and guidelines. In principal, the LCA encompasses four phases:

- Definition of the goals and scope – to provide description of a product system in terms of system boundaries and a functional unit that defines the function of the given product system

- Development of life cycle inventory (LCI) – to collect data and provide calculation procedures for quantification of relevant inputs (e.g., material inputs) and outputs (e.g., emissions to air), considering a product system from cradle to grave
- Life Cycle Impact Assessment (LCIA) – to aggregate the results from the inventory analysis and to evaluate the significance of the product's potential environmental impacts. This process involves connecting inventory data with specific environmental impact categories and the respective category indicators, such as the global warming potential as an indicator for climate change
- Interpretation of the assessment – to consider the findings both from LCI and LCIA to provide conclusions and recommendations.

Assessing nanotechnology and nanoproducts with LCA gives an opportunity for proactive action by different stakeholders to prevent or minimise potential adverse effects to human health and the environment over the entire life cycle of nanoproducts. In the case of toxicological safety, LCA can add supplementary environmental information to support decisions on the development of certain nanomaterials or nanoproducts (Klöpffer et al., 2007). It is, however, of note that LCA is not a tool for carrying out exposure assessment. It is merely the other way around, i.e. that exposure assessments can provide information to LCA relevant for impact assessment of nanoparticle releases. LCA can nonetheless be helpful in identifying the stages in the life cycle during which exposure may be relevant. This study did not follow all the steps of an LCA for the reasons that it would need a far longer-term project, and a good database, which is currently not available for nanotechnologies and CNTs. The LCA approach adopted in the study is thus a simplified approach focusing primarily on illustrating the potential for inhalation exposure during the life cycle.

Sections 4.1 to 4.6 show how the ISO standards and other recommendations for LCA relate to exposure potentials in LCAs in general, and more specifically which issues are relevant for LCA of nanotechnologies. Section 4.7 discusses the three case studies; CNT in batteries, in textiles and in epoxy resin.

4.1 ISO Standard and other recommendations

The relevant ISO protocols have been studied with particular emphasis on how the principles and guidelines for LCA can support exposure assessment of products that contain engineered nanoparticles (ENPs) in general, and carbon nanotubes (CNTs) in particular. In the current format, the ISO protocols for LCA are not intended to present a framework for exposure assessment. Especially the ISO 14040, which provides the principles and the general framework for LCA, does not provide any guidance or requirement concerning the exposure assessment of humans or the environment during the life cycle of materials or products.

In this regard, a workshop sponsored and organised by Woodrow Wilson Institute for International Scholars and the EU Commission held in Washington 2-3 October 2006 (Klöpffer et al., 2007) has already discussed the extent to which the ISO protocols are sufficient for nanotechnology products, and whether any amendments would be needed. It was concluded that the ISO-framework for LCA is fully applicable to LCA of nanomaterials and nanoproducts. In some phases and steps, however, there are a number of issues that need to be addressed in more detail. These include, for example:

- that nanoproducts may have functions that are quite new, and for which it may be difficult to specify a functional alternative,

- that the inventory may be difficult to develop due to rapidly evolving production technologies, and in particular
- that the impact assessment of risks of nanoparticles is difficult due to the lack of data for release exposure and effects of nanoparticles.

In relation to exposure assessment, the functional unit is not relevant as such (only relevant for comparative purposes), but both the inventory and the impact assessment may be relevant to study. The inventory provides information about releases in the different life cycle stages whereas the impact assessment aims to cover the cause-effect relationship from the release to the effect (or impact) on human and/or the environment.

Generally, the goal and scope definition must be clearly defined and consistent with the intended application of the study. In the scope definition, the following items must be considered and clearly described (ISO 14044, 2006):

- the product system to be studied;
- the functions of the product system or, in the case of comparative studies, the systems;
- the functional unit;
- the system boundary;
- allocation procedures;
- LCIA methodology and types of impacts;
- interpretation to be used;
- data requirements;
- assumptions;
- value choices and optional elements;
- limitations;
- data quality requirements;
- type of critical review, if any;
- type and format of the report required for the study.

Some of these items are described in more detail in the standard. In this project, where the goal is to exemplify the use of LCA as input for the inhalation exposure assessment, it is for example important that the system boundaries include processes in which there may be a significant potential for exposure to nanoparticles and CNT. Omission of unit processes is only allowed to the extent that the omission does not change significantly the conclusion of the study. It should for example be specified which inputs and outputs are included in the study (or which criteria are used to determine their significance (make cut-offs), e.g. mass, energy or environmental significance. In the definition of scope it must additionally be specified which impact assessment methodology and type of data will be used. So when dealing with nanotechnologies it must already be specified in the scope definition whether or not potential impacts of nanoparticles are included in the assessment, and if included which requirement for data and impact assessment this decision poses to the study. LCAs are of an iterative nature as also illustrated for the inventory analysis in Figure 3, which means that the initial requirements etc for study are defined in the scope but these can be subject to change as the study progresses.

In the ISO 14044, which provides the requirements and guidelines for LCA, chapters are dedicated to the inventory and the impact assessment, respectively.

When executing the plan for inventory analysis the operational steps in Figure 3 should be performed (note that not all iterative steps are included in the figure) (ISO 14044, 2006).

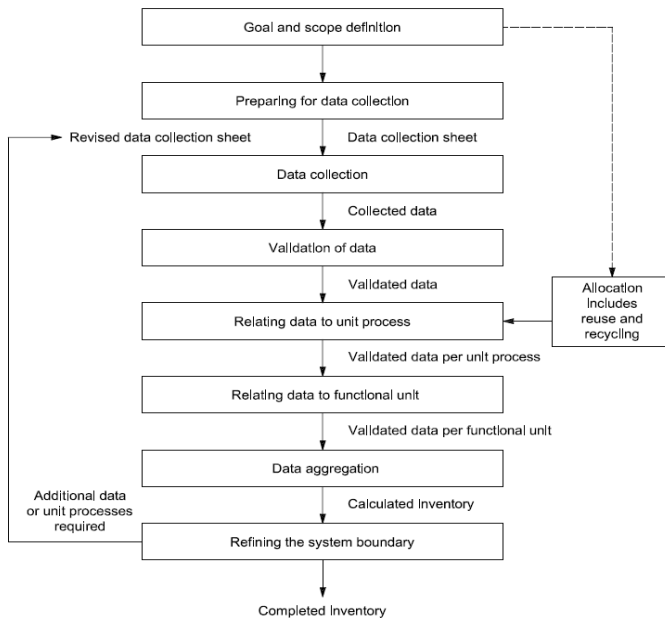


Figure 3: Simplified procedure for inventory analysis (ISO 14044, 2006)

The qualitative and quantitative data shall be collected for each unit process that is included in the system boundaries. Measures should be taken to ensure uniform and consistent understanding of the product system to be modelled. These measures include the following (ISO 14044, 2006):

- drawing unspecific process flow diagrams that outline all the unit processes to be modelled, including their interrelationships;
- describing each unit process in detail with respect to factors influencing inputs and outputs;
- listing of flows and relevant data for operating conditions associated with each unit process;
- developing a list that specifies the units used;
- describing the data collection and calculation techniques needed for all data;
- providing instructions to document clearly any special cases, irregularities or other items associated with the data provided.

The major headings under which data may be classified include (ISO 14044, 2006):

- energy inputs, raw material inputs, ancillary inputs, other physical inputs,
- products, co-products and waste,

- releases to air, water and soil, and
- other environmental aspects.

Within these headings, individual data shall be further detailed to satisfy the goal of the study.

Thus the specification of data collection (inventory) in the ISO protocol does not entail any requirements to include data that supports a more specific exposure assessment, unless it is specified in the goal and scope of the study.

The Life Cycle Impact Assessment (LCIA) also does not specifically address such aspects. For LCIA it is important to realize that it is different from other techniques such as e.g. risk assessment since it is a relative approach based on a functional unit (see. eg. Olsen et al, 2001) although LCA may use data gathered by other techniques.

The LCIA phase shall be carefully planned to achieve the goal and scope of an LCA study. The LCIA phase shall be coordinated with other phases of the LCA to take into account the following possible omissions and sources of uncertainty (ISO 14044, 2006):

- whether the quality of the LCI data and results is sufficient to conduct the LCIA in accordance with the study goal and scope definition;
- whether the system boundary and data cut-off decisions have been sufficiently reviewed to ensure the availability of LCI results necessary to calculate indicator results for the LCIA;
- whether the environmental relevance of the LCIA results is decreased due to the LCI functional unit calculation, system wide averaging, aggregation and allocation.

Four stages of the impact assessment are distinguished: classification, characterization, normalisation and weighting. Classification concerns the assignment of LCI results to the impact category, i.e., the data from the inventory table are grouped together into a number of impact categories. The characterization is the actual calculation of category indicator results and concerns the analysis and estimation of the magnitude of potential impacts on the ecological health, human health or resource depletion for each of the impact categories. Each emission will contribute differently to the impact categories depending on the specific substance properties and thus has a distinguished characterization factor that quantifies the impact potential per kilogram of substance. Normalization and weighting are optional and will not be further explained here.

For each impact category, the necessary components of the LCIA include (ISO 14044, 2006):

- identification of the category endpoint(s),
- definition of the category indicator for given category endpoint(s),
- identification of appropriate LCI results that can be assigned to the impact category, taking into account the chosen category indicator and identified category endpoint(s), and
- identification of the characterization model and the characterisation factors.

Specifically, it is mentioned that the environmental mechanism and characterisation model that relate the LCI results to the category indicator and provide a basis for characterization

factors shall be described. Additionally, the appropriateness of the characterization model used for deriving the category indicator in the context of the goal and scope of the study shall be described.

An example of the cause effect chains considered in LCA is illustrated in Figure 4. Here it is illustrated that LCIA models the entire chain from the emission till either mid-point or endpoint. This means that fate, dispersion etc. are all included in the characterisation model for the particular impact category. It is stated specifically in the standard that the environmental relevance of the category indicator or characterization model should be clearly stated in the following terms (ISO 14044, 2006):

- the ability of the category indicator to reflect the consequences of the LCI results on the category endpoint(s), at least qualitatively;
- the addition of environmental data or information to the characterization model with respect to the category endpoint(s), including
 - o the condition of the category endpoint(s),
 - o the relative magnitude of the assessed change in the category endpoints,
 - o the spatial aspects, such as area and scale,
 - o the temporal aspects, such as duration, residence time, persistence, timing, etc.,
 - o the reversibility of the environmental mechanism, and
 - o the uncertainty of the linkages between the category indicators and the category endpoints.

Obviously, the formulations in the standard are rather general even if they specify the requirements of the LCIA. However, for a specific impact category as toxicity to human there are no specific requirements as how exactly to perform the assessment. The European Commission has very recently put a technical guidance document in stakeholder hearing that describes and recommends specific methodologies for performing the LCIA. How recommendations are for toxicity to humans will be elaborated later.

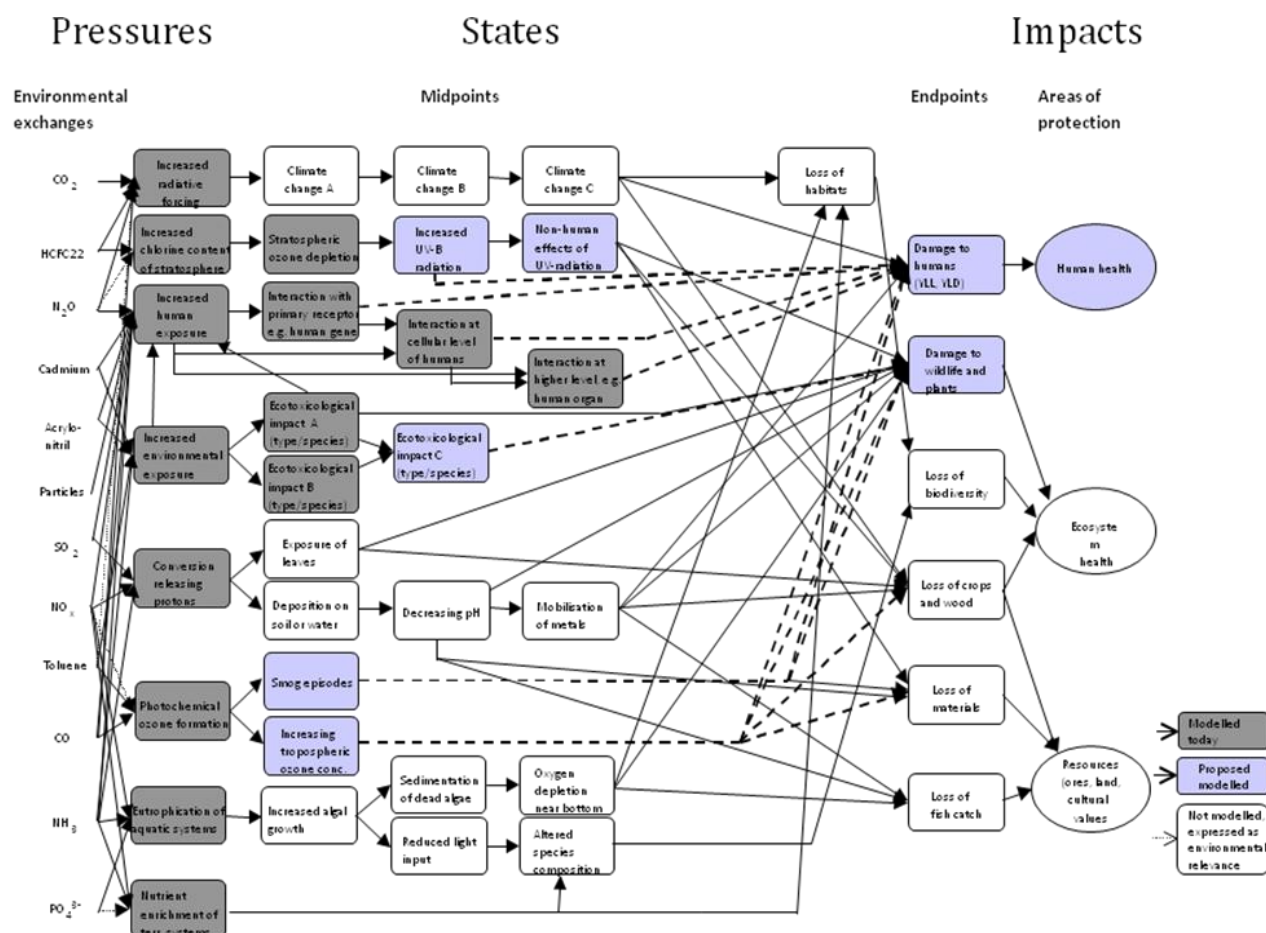


Figure 4: Cause effect chains in LCIA (Modified and updated after Wenzel et al., 1997)

To sum up the requirements in the ISO protocol the specification of data collection (inventory) does not entail any requirements to include data that supports a more specific exposure assessment, unless it is specified in the goal and scope of the study. Likewise for the LCIA no specific requirements are given relating to the methodology used to assess the impacts. Even though the overall framework of the ISO protocols can be applied to nanotechnologies it does not give good recommendation on how to deal with the particular issues related to nanotechnology e.g. exposure to particles in the life cycle.

4.2 International Reference Life Cycle Data System (ILCD) Handbook

In a draft guidance document for public consultation, the European Commission aims to set up a framework and requirements for Life Cycle Impact Assessment (LCIA) models and indicators (TGD, LCIA, 2009). No commonly accepted set of data nor methods for Life Cycle Impact Assessment (LCIA) exist and the Guidance Document provides the general framework and methodological requirements for the environmental impact assessment for use in LCA, as outlined in general terms in ISO 14044. Traditionally, as in many other environmental assessments, LCIA uses linear modelling and takes the effects of the substances into account, but not their background concentrations and the geographical dependency on fate. The method aggregates the environmental consequences over release points in time, release locations and substances (chemicals). This allows calculating potential impact scores, which reflect contributions to environmental burdens. This can be different from RAs that aim to ensure the safety of people or the environment and to identify the risks

due to a certain activity in a specific site or region and in a given time period. Risk assessment can therefore take a conservative approach. LCA, on the other hand, is a comparative framework in which it is essential that the potential impacts be compared on a realistic basis. Additionally, LCIA has a broad scope in terms of impacts covered, whereas RA has a clear focus on chemicals and their effects on the environment and human health.

The TGD address 11 impact categories of which particularly human toxicity and respiratory inorganics/particulate matter are relevant to this project. For human health in general the use of the DALY³⁵-concept is recommended as a default indicator basis for human-health for environmental assessments for use in Life Cycle Assessment, including years of life lost for mortality and years of life disabled for morbidity, without age weighting and discounting.

Concerning human toxicity it is stated that “LCA characterisation models and factors for toxic effects must rely on models that account for a chemical’s fate in the environment, human exposure, and differences in toxicological response (both likelihood of effects and severity).” Concerning human toxicity it is stated that “LCA characterisation models and factors for toxic effects must rely on models that account for a chemical’s fate in the environment, human exposure, and differences in toxicological response (both likelihood of effects and severity).” Figure 5 illustrates the models that ideally should be considered for each emission/release from a unit process in the LCIA of human toxicity. Currently, operational methods for assessing indoor air exposure at home or in the workplace have not been fully developed (see also chapter 4.3 below).

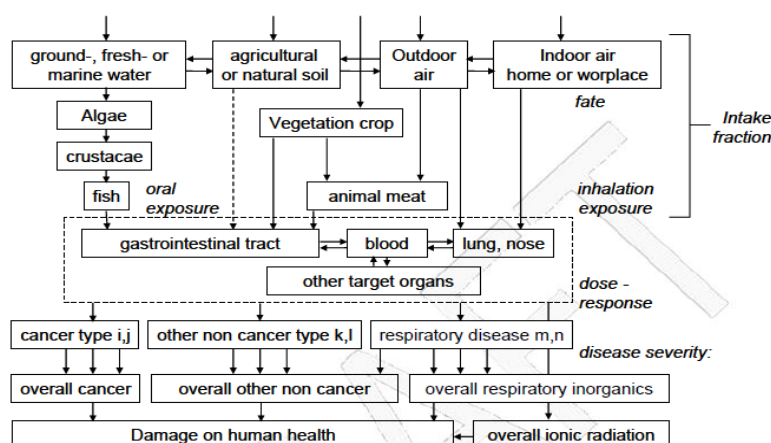


Figure 5: Environmental mechanisms for the human toxicity effects (TGD LCIA, 2009)

Contributions of emissions to short-term/acute and local scale effects are presently not addressed in the TGD, including those associated with indoor exposures, direct exposure to products during their use stage, and to exposures in the work place, focussing on the contribution of emissions to the risk of toxicological impacts and associated consequences considering the entire human population and disperse emissions. Thus, even in the most recent recommendations for LCIA of human toxicity some of the most relevant human exposure routes to CNT and nanoparticles (consumer and work place exposure) are not addressed.

³⁵ The Daly Concept (Disability Adjusted Life Years) combines information on quality of life and life expectancy in one indicator, deriving the (potential) number of healthy life years lost due to premature mortality or morbidity. Morbidity is weighted for the severity of the disorder (Murray and Lopez, 1996).

The TGD also includes a recommendation for respiratory inorganics/particulate matter, which could perhaps be even more relevant for CNT and nanoparticles. However, also here the focus is on the increase in ambient concentration and the resulting effects. The main reason for the distinction between human toxicity and particulate matter is the differences in fate and exposure modelling but also to some degree the difference in dose-response. For example, formation of secondary particulate matter is considered (TGD, LCIA, 2009).

4.3 Indoor and workplace exposure

Methodologies for including indoor and workplace exposures in LCIA are still in their infancy. Methods for including work environment have not really been able to address the exposure issue, the main problem being that exposures in the workplace are not necessarily related to a specific production line (e.g. a worker on one production line may easily be exposed to releases from another production line). Therefore, impact assessment of work environment has been related to accident statistics within branches/industries.

For indoor exposures a working group in the UNEP/SETAC life cycle initiative has recently proposed a methodological framework (Hellweg et al., 2009) that takes origin in exposure models for occupational hygiene and indoor air quality studies. They suggest several models for calculation of indoor exposure concentrations from a simple 1-box model to an eddy-diffusion model depending on the number of sources and mixing conditions in the room. For the use in the current project the methodology is still not operational so even though it is shown that indoor exposure have a very significant importance in the human health impacts assessment compared to outdoor exposures it is not yet possible to include within the timeframes available.

4.4 Nanotechnology and LCA workshop

The workshop co-sponsored by the Woodrow Wilson Center for International Scholars and the European Commission (Klöpffer et al., 2007) also concludes that the ISO standards are appropriate for LCA of nanotechnologies, but that the main problem is lack of data and understanding in certain areas.

The main barriers for conducting LCAs in the nanotechnology field are essentially the same as those in all other fields. The first barrier is the necessity to increase awareness of applying the life cycle concept in order to avoid the unintended shifting of environmental burdens. The second main barrier is the lack of reliable inventory (input and output) data as well as data on impact relationships. Proprietary information on manufacturing processes, the absence of toxicological test results, a general lack of data and wide process-to-process variation are other examples of the barriers for all LCA work. As mentioned above in some phases and steps there are a number of issues that need to be addressed in more detail. The focus here will be on:

- that the inventory may be difficult to develop due to rapidly evolving production technologies, and in particular
- that the impact assessment of risks of nanoparticles is difficult due to the lack of data for release, exposure and effects of nanoparticles.

As nanoproducts are only starting to enter the market, it is at present unclear how processes related to use, maintenance and end-of-life services (e.g., disposal, recycling) will proceed. Some materials will be released during use, either intentionally (e.g., nano-additives in

gasoline) or unintentionally (e.g., nano-additives in tires). Exact release rates are not always available, especially when these are condition-dependent (e.g., when they depend on the driving style of the car driver or on the weather). The behaviour of nanomaterials that have been discarded after use is also not yet clear. For instance, their reaction with other materials in an incinerator or at a dump site is uncertain, yet these are required data in an LCA study.

To discuss the inventory further, it should aim to provide information that is appropriate to carry out a following LCIA as stated in the ISO 14044. When CNT or, more generally, nanoparticles are released exactly what should be measured in order to be able to carry out an impacts assessment? In standard LCI tables, only the quantity and the chemical composition of releases are reported. For instance, a typical inventory contains items such as “12 kg CO₂” and “0.36 kg 1,1,1-trichloroethane.” Only for some chemicals an additional characteristic is required, for instance, its isotope (for radioactive releases), its stereo-isomer (for a chemical like cyclohexane) or its valence (for an ion such as chromium). For nanoparticles that are released during any life-cycle stage, additional parameters will be of importance in the impact assessment (either for fate, exposure or effect modelling). Parameters that most likely influence toxicity of nanomaterials include the chemical composition, particle size, shape, aspect ratio, crystal structure, surface area, surface chemistry and charge, solubility, as well as adhesive properties. As nanoparticles may also be coated, it is important to find out whether to report the pure material or the composite. In this context, it is also important to know whether nanoparticles change their form (shape, coating, etc.) during their life cycle, for instance, due to aging and other influences such as weather, mechanical stress/pressure, electromechanical fields or catalysis. As a result, the elementary flows characterizing nanomaterials in the inventory may require that these additional characteristics be described. (Klöpffer et al., 2007).

Overall, the workshop concluded that the UNEP/SETAC framework (Udo de Haes et al. 2002) for toxic impacts (as illustrated in Figure 6) can, in principle, be used for specific impacts caused by nanoparticles and nanoproducts given that (nanomaterial-specific) fate, exposure and effects have been adequately identified. Examples of some considerations that must be taken into account include (Klöpffer et al, 2007):

- Traditional dose-response relationships based on mass or dose will not suffice since impacts may be linked to other aspects of the nanomaterials, e.g., surface area, chemical composition, particle size, shape and others;
- Transformation and structural changes could occur in the environment after release;
- Dermal uptake may have significance and should be covered for relevant applications;
- Fate and exposure models and Physiologically Based Pharmacokinetic Models (PBPK) based on basic nanoparticles properties (e.g., fullerene partition coefficients) may be useful to predict exposure;
- It may be useful to differentiate between bioactive and non-bioactive nanoparticles;
- It is an open question how to deal in toxicology with structural/physical mechanisms rather than chemical interactions/virus or enzyme-like behaviour (which do not fit into classical toxicological models); and
- There may be synergistic or antagonistic interactions between nanomaterials and existing sources of environmental impacts such as current chemicals.

It will be noticed that the consideration necessary for LCIA of nanoparticles are quite the same as those questions that to a large extent are still open when discussing risks of nanomaterials.

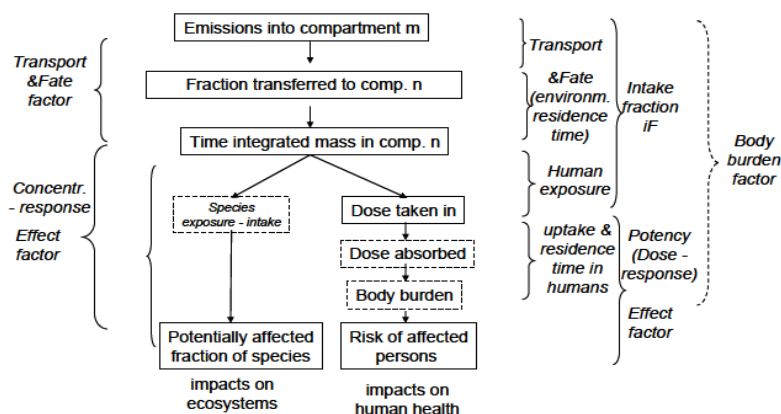


Figure 6: The UNEP/SETAC framework for assessment of toxic impacts (Jolliet et al., 2004)

4.5 NanoImpactNet Nano Life Cycle Workshop

Within the Nano Impact Net project (EU FP7 funded) a workshop was held in Zürich 4-5 September 2008 with a focus on Life Cycle of nanomaterials. The workshop resulted in a paper (Som et al., 2009)³⁶ where the applicability of different environmental management tools was scrutinised. Under the overall umbrella of “life cycle concepts”, an important distinction is made between the formal ISO framework of LCA and other life cycle based tools and it was attempted to characterise the different tools based on what type of information they can provide. This is shown in the table in appendix 1. From this table it can be seen that the formal LCA potentially (depending on the information available) can provide information on future nano-applications and – products, release scenarios for nanoparticles, relative impact of nano-products on human health and environment, and opportunity for material and energy saving or risk for increased material consumption. The particular strength of LCA is that it embraces, in principle, all environmental impacts and thus can avoid a problem shifting. But it can also be seen that most exposure related information can be better retrieved by other tools.

4.6 Summary of LCA recommendations and standards in relation to exposure

It is clear from the overview given above that LCA is not a tool for exposure assessment. The ISO protocols require that the scope of LCA shall cover all parts of the life cycle that can have a decisive influence on the results. Unless potentially toxic impacts of nanoparticles or CNT are deliberately and arguably left out of the scope, their release during some life cycle stages should be included considering that they may have a significant human health impact. The impact assessment part of LCA, LCIA, should be able to make a plausible model for the cause effect chain comprising a transport and fate factor, human exposure, and the dose-response of the causing agent. However, as for Risk Assessment, there are still many unknowns that make a proper impact assessment difficult.

³⁶ Som, C., Berges, M., Chaudhry, Q., Dusinska, M., Fernandes, T.F., Olsen, S.I., Nowack, B. (2009: In Press) The importance of life cycle concepts for the development of safe nanoproducts, Toxicology.

Nonetheless, LCA may still be useful since no other environmental management tool aims to include all environmental impacts in the whole life cycle of a product. LCA can thus answer more broad question about the environmental performance of nanotechnologies and nanotechnological products, for example, (Klöpffer et al., 2007):

- How do the life cycles of devices/products using nanomaterials compare with those of conventional devices/products? To what extent do savings in energy efficiency compared to those of conventional devices/products balance the energy consumption used in producing nanomaterials?
- Which specific phase in the life cycle (e.g., manufacturing, end-of-life) dominates energy use?
- Are there any issues in end-of-life management that are specific to nanomaterials, especially recovery and reuse or recycling?
- What are the key eco-toxicity and human-toxicity potentials for nanomaterials?
- How do we integrate toxicological RA methods into LCA for nanomaterials?
- Are there trade-offs between potential eco-toxicological and human toxicity impacts and a potential environmental gain related to global change and other pressing environmental problems?
- What are the geographical impacts of devices/products using nanomaterials compared to those of conventional devices/products?

4.7 Case studies

Three study products were selected for exposure analysis in this project. Considering the current and projected large-scale use of CNTs, the products identified for the study included batteries (rechargeable, secondary), textiles (made of CNT fibre, or coated with CNTs), epoxy resin based adhesive formulations.

The case studies were performed using life cycle perspective, focusing on the exposure potential to CNT during the life cycle of the selected products. Because it was in the remit of this project to gather primary data, the study is based on the data available in literature. The study, therefore, performed literature searches to inform the LCA. An overview of relevant literature in relation to exposure potentials and energy use in raw materials, manufacturing, use and disposal stages, respectively is given in appendix 2. One published article by Köhler et al. (2007) was found to be particularly relevant as it reports a study of the potential release of CNT throughout the application life cycle for Li-ion batteries (with CNT) and for textiles.

4.8 Raw materials and manufacturing

The raw materials stages, i.e. including the manufacture of CNT, are identical for all three cases since our focus is on CNT exposure potential (other parts of the raw materials stage will of course differ since one case will require the production of textiles and another the production of resins). The production pathways of CNT are discussed elsewhere in this report (see section 3.2). Several papers study the energy requirements for production of CNT but only a few of them include any information on the potential releases and consequent exposure potentials.

Energy consumption in the production of CNT is generally considered to be very high but differs considerably between different studies. It ranges from 144 GJ/kg CNT for HiPCO

production pathway to 880 GJ/kg for CVD production pathway (both including purification (Healy et al., 2008). Kushnir and Sandén have estimated considerably lower (but still high) energy uses ranging from 482 MJ/kg CNT for the CVD process to 9.6 GJ/kg CNT for laser ablation process. However, these numbers are strictly based on the cradle to gate study of 1 kg of CNT. The actual use of CNT in each product (per functional unit) may be very small thus lowering the energy consumption per functional unit. Khanna and Bakshi (2009) calculate that based only on the cradle to gate of a nanocomposite polymer (e.g. epoxy resin) the energy consumption is 1.3-10 times higher than steel (considering same functional unit, including stiffness) but again they have not taken into account that there might be significant energy saving in the use stage (e.g. reduced fuel consumption of a car due to lower weight of the car using nanocomposite polymers).

Concerning exposure potentials in the production stage Healy et al. (2008) emphasise the need for more data to enable assessment of impacts of worker exposure. Köhler et al. (2007) discuss qualitatively the exposure potentials. The gas phase processes may result in possible leakages if there is a positive pressure in the reaction vessels but not as probable if vacuum exists; vapour phase processes are not likely to result in direct releases; The recovery phase, which may be in bag-filters there is a risk of re-suspension of CNTs (most probable as agglomerated bulk powder) and also in the cleaning and maintenance of the machinery there may be exposure potentials.

The manufacture of batteries and textiles are specifically discussed in Köhler et al (2007) but no specific information has been available for epoxy resins. For the batteries, there is a potential exposure in all stages of manufacturing until the cells are sealed. Also production waste and contaminated facilities might be a source of CNT releases. In the textiles production (a complete overview of the use of nanoparticles in textiles is given in Som et al. (2009b)) there are potential releases in the early stages of manufacturing when the polymers are blended with CNT and in the fabric finishing and tailoring (due to dry and wet abrasion of fibres).

No studies on epoxy resins have been identified, but it can be assumed that the exposure potential is the same as for textiles i.e. that there may be a release potential until the CNTs are blended into the resin and that there may be a further potential for release of resin particulates containing CNT during finishing (e.g. grinding).

4.9 Use stage

The energy consumption in the use stage is very scarcely covered in any of the studies identified. Bauer et al. (2007) find that Field emission displays (FED) have significant energy savings in the use stage compared to the wide spread LED technology. But the remainder is mostly estimates (e.g. Lloyd and Lave, 2003).

Only very few studies have dealt with the exposure potential in the use stage of products containing CNT. Again Köhler et al. (2007) is the most complete study looking into batteries and textiles. No studies on epoxy resins have been identified.

If properly handled the release from batteries is unlikely in the use stage due to the encapsulation of CNTs.

In textiles CNTs are very stable and their potential release depends on the degradation of the matrix material. The release depends on the binding of ENP and on influences on the textiles during its life cycle, e.g. mechanical stress, washing, UV-light, solvents etc. The ENP can be

released as single ENPs, agglomerated ENPs or nano- or micro meter scale textile containing ENP (Som et al., 2009b).

4.10 Disposal stage

The disposal stage is also primarily covered by Köhler et al. (2007) but also by Olapiriyakul and Caudill (2008). The latter mentions an increased energy use (about 1/3) in the disposal stage in order to ensure oxidation of the CNTs during incineration. This is in correspondence with an earlier paper (Cataldo, 2002) where it was shown that CNTs requires rather high temperatures to oxidise.

Exposure potentials depend on the process details for the disposal. Some technologies may imply shredding, milling and thermal processing which may result in high exposure potentials if not in enclosed processes, with a potential occurrence in the exhaust of the recycling facilities because filters are not designed for nanoparticles. Manual dismantling may cause release of CNT and direct exposure of workers. Mechanical processing and pyrolysis do not eliminate CNTs and may be a source of release because handling takes place outside controlled environments (Köhler et al., 2007). For textiles (in recycling) a cross contamination may occur (if downcycling to technical products).

CNTs are considered to be incinerated under high temperatures but densely packed CNTs might survive incineration and be collected in the filters together with other dust and enter either the slag or the flue gas cleaning products. In landfills there is a risk of leakages due to battery corrosion.

For epoxy resins, even though not mentioned in any references, it can again be assumed that they will act like the textiles since it is a polymer containing nanoparticles.

5.0 Estimation of the likelihood of inhalation exposure to CNTs

5.1 Background

The risk of health effects that may arise in an individual or a population as a result of exposure to any chemical agent, is generally considered to be a function of the intrinsic harmfulness of the chemical (its hazard or toxicity) and the dose (amount) which accumulates in the specific biological area of interest. In an occupational context, it is unusual to be able to quantify the dose, specifically in the case of insoluble particulates and fibres. In order to quantify and manage the risks, it is usual to use exposure as a proxy for dose.

Critical questions in relation to exposure are how much, how long and how many people might be exposed. Thus, exposure is usually measured (quantified or assessed) in terms of its intensity (concentration) and duration (or frequency). Control of exposure (to zero) effectively removes the risks from the toxic agent. Without exposure there is no risk.

Maynard et al. (2004) was the first to report exposures during production and handling of CNT. Maynard carried out a field study in which airborne and dermal exposure to single walled carbon nanotubes (SWCNT) were investigated while handling unrefined material. This was complemented by a laboratory based study to evaluate the physical nature of the SWCNT aerosol formed during mechanical agitation.

Methner et al. (2006, 2007) reported the “Identification and characterization of potential sources of worker exposure to carbon nanofibres during polymer composite laboratory operations”. The study considered various operations involved in the handling or processing of carbon nanofibre (CNF) materials to determine whether emission of these materials occurred. Mean concentrations of $64 \mu\text{g m}^{-3}$ for weighing operations and $93 \mu\text{g m}^{-3}$ for mixing with a solvent were reported. Notably, wet sawing of composite material and transferring carbon nanofibres to a mixing vessel were observed to elevate the airborne particle mass concentration compared to background levels, although the investigators could not conclude whether exposure was excessive or a health hazard existed in the absence of occupational exposure limits for carbon nanofibre and clearly defined health effects. At the time, the investigators recommended the use of interim precautionary measures (worker education, engineering controls, use of good practice to minimise exposure etc) prior to further information on the health risks and extent of occupational exposure to nanomaterials becomes available.

Han et al. (2008) monitored the possible exposure to MWCNT release in a carbon nanotube research laboratory. To estimate the potential exposure of researchers and evaluate the improvement of the workplace environment after the implementation of protective control measures, personal and area monitoring were conducted where the researchers handled unrefined materials. Measurements were made in the post production recovery of MWCNT, processing and in a blending activity, part of a composite formulation process. Mass concentrations of up to 0.43 mg m^{-3} were reported during blending before exposure control was implemented. Following implementation of exposure control (hood and ventilation), the maximum measured concentration (mass) was 0.04 mg m^{-3} . Even without exposure control, mass concentrations during production were not detected and during weighing were low (0.1 mg m^{-3}). This study is the first which has attempted to quantify release using methodology which is consistent with that recommended by WHO for other fibres. Han adapted the method to count fibres using a TEM. It is not clear from the paper, nor from subsequent discussions with the author, the extent to which all of the counting rules relevant to WHO have been applied. For example, many of the images in the paper show clumped or overlapping fibres. No comment is made in the paper as to how such aggregates were dealt with. Fibres were only found in the blending scenario and were found on both personal and area samples at approximately the same level. The reported number concentration was very high (193.6 and $172.9 \text{ fibre ml}^{-1}$). These are two orders of magnitude greater than typical asbestos workplace exposure limits of $0.1 \text{ fibre ml}^{-1}$. Enclosure of the blending activity reduced the fibre count by four orders of magnitude, indicating effective control of fibre release. Interestingly, following the installation of engineering measures where weighing was carried out, one sample showed a fibre concentration of $1.99 \text{ fibre ml}^{-1}$. It is important to note however that all of the fibres counted were short. The reported maximum size of fibres observed was 1500 nm , which would be too small to be considered a fibre under the WHO criteria, where the minimum size of a fibre is 5000 nm (i.e. if counted under strict WHO rules), the fibre count would be zero.

In Bello et al. (2009), exposure to nanoscale particles and fibres during machining of hybrid advanced composites containing carbon nanotubes (as produced in Bello et al 2008) was examined. This study investigated airborne exposures to nanoscale particles and fibres generated during dry and wet abrasive machining of two three-phase advanced composite systems containing carbon nanotubes (CNTs), micron-diameter continuous fibres (carbon or alumina), and thermoset polymer matrices. Measurements were made of airborne

concentrations at sources and in the breathing zone of workers. This is the only study which has reported surface area concentrations. Significant exposures to nanoscale particles compared to background were generated during dry cutting of all composites. Elemental composition of these particles matched reasonably well the expected composition of processed composites. Submicron and respirable fibres were generated from dry cutting of all composites. The base–alumina and CNT–alumina composites generated about 1.6 respirable fibres cm^{-3} , ~2.4 times less than the base–carbon composites. No obvious differences were found in the behaviour of base- and CNT-composites with regards to their tendency to generate respirable fibres and particles. Breathing zone concentration of respirable fibres (~0.2 fibres cm^{-3}) are still of concern in spite of these concentrations being an order of magnitude lower than source concentrations. Importantly, sub-micron long, thin (5–20 nm diameter) and sharp, needle-like fibres were also found for all composites. Although they could not be quantified, such fibres were common. Fibre morphology and elemental composition suggest they may be originating from two distinct processes: fracturing of advanced fibres along their axis or perpendicular to it, and fracturing of the CNT composite at the interface. Wet cutting in all, but one test (broken guard) reduced exposures to background levels. In one test, during which the guard around the rotary wheel was visibly damaged, wet cutting generated significant airborne exposures compared to background. Although airborne particulate matter was clearly emitted during this test (as confirmed by deposition of black aerosol on surfaces) and the size distribution was distinct from dry cutting it is unclear how much of that aerosol was water.

5.2 Appraisal of the exposure potential to CNT in products

Incorporation of CNT into products provides the possibility of enhanced properties and functionality and is being actively pursued. Desirable properties include high tensile strength providing reinforcement and increased wear resistance, electrical conductivity providing antistatic, shielding of EMF and possible sensing capabilities, thermal conductivity providing dissipation of heat or flame retardancy and the possibility of “intelligent” textiles (Kohler et al 2008). However, current use of CNT in the development in many products is still primarily at a research stage due to still high cost of CNT and technical issues.

Carbon nanotubes are added to the carbon electrodes in lithium ion rechargeable batteries to improve the performance of the battery. A typical nanotube loading in the carbon electrode is 10 wt% of the electrode.

For composites, there are two main applications for nanotubes: matrix modifiers using the CNTs to change the thermal, electrical and rheological properties of the matrix, and reinforcement using the CNTs to improve the mechanical properties of a polymer. There has been a substantial amount of literature and even commercial applications on nanotubes as matrix modifiers to improve the electrical properties of a polymer. The literature was reviewed recently by Baunhofer et al (2009) who found that minimum concentration needed to achieve a useful increase in electrical conductivity of the composite varied from 0.002 to 5% w/w. It should be noted that the wide range of values for the percolation threshold in the literature are due to the differences in polymer, nanotube type and processing conditions. Commercial product literature suggests that a concentration of 7.3% w/w is recommended for anti-static additives. There is a major research focus on trying to realise excellent mechanical properties with low nanotube loadings. However, the closest to market contains ~ 60% v/v

carbon nanotubes, assuming a similar loading to that used in the conventional fibre composites.

For textiles, two types of processes have been considered. Firstly, the integration of CNT (both SWCNT and MWCNT) into the synthetic polymer fibres. This can be achieved by in situ polymerisation of a mixture of monomer and CNT or by dispersion of CNT in molten polymer. The resultant mix is then spun to produce a synthetic fibre with CNT integrated into the structure. This synthetic fibre is woven to produce textiles clothing etc. at the start of the process. Secondly, coating of synthetic or natural fibres with CNT usually by immersion in a bath or coating finished textiles or clothing by immersion, spraying or printing.

For the products considered in this study, we have identified and appraised the exposure potential for a comprehensive set of activities across the product life cycle, including occupational, environmental and consumer exposure scenarios. The appraisal highlights the possible sources of exposure, influencing factors and the available contextual information on particle/fibre production to rank the exposure potential.

The exposure ranking used in the assessment is based on consideration of the potential for exposure to CNT and the availability of supporting evidence in the literature. The binary rank is constructed using the following matrix:

		Level of Evidence		
		1. Evidence in the literature, specific to CNT	2. Analogous evidence in the literature, not specific to CNT	3. No evidence able to be sourced
CNT release characteristics	A. Deliberately aerosolised CNT, with potential for inhalation exposure.	A1	A2	A3
	B. Free CNT, with potential for inhalation exposure.	B1	B2	B3
	C. Matrix-bound CNT particulate, with potential for inhalation exposure.	C1	C2	C3
	D. Matrix-bound CNT, with minimal potential for inhalation exposure.	D1	D2	D3

NB. The ranking is intended only to assist in our qualitative assessment and comparison of relative risks across and between the activities and products, as shown in the summary Table.

5.2.1 Carbon Nanotubes in Li-ion Batteries

Activity Class	Activity	Material	Exposure group	Exposure ranking
<i>Manufacturing</i>	<i>Pre-cursor CNT material preparation</i>	<i>CNT, semiconductor-CNT composites, functionalised MWCNT or SWCNT</i>	<i>Occupational</i>	<i>B1</i>
It is anticipated that processes involving the preparation of CNT-containing pre-cursors, prior to the dispersion of CNTs in solvents or electrolytes, may generate particulate emissions of CNTs, CNT-composites, or their aggregates. These include material decanting, mechanical milling, and mixing. Factors that can be expected to influence the potential for release and inhalation exposure to CNT include the physical state of the CNT material as-supplied (e.g. powder, dispersion, pre-mixed batches), quantities to be handled, anticipated dustiness of the processes, process containment and particulate control measures in place (e.g. ventilated enclosures or LEV). There is no published evidence of release in this specific scenario, however mixing tasks in other settings have demonstrated release potential of CNT (e.g. Maynard et al 2004, Han et al 2008).				
<i>Manufacturing</i>	<i>Electrode manufacturing prior to battery sealing</i>	<i>Fixed CNT, semiconductor-CNT composites, functionalised MWCNT or SWCNT</i>	<i>Occupational</i>	<i>C3</i>
It is anticipated that electrode preparation processes involving CNT pre-cursors may generate particulate emissions of CNTs, composites or their aggregates if processes are capable of aerosolising materials. These processes may include the preparation of electrode materials, slurry preparation, electrode assembly and disposal of any waste materials. Factor that can be expected to influence the potential for release and inhalation exposure to CNT include the quantities of CNT-containing material being handled, the anticipated dustiness of the processes, process containment and particulate control measures in place (e.g. ventilated enclosures or LEV). However, no public domain data is available currently on the potential release of CNT from such situations.				
<i>Manufacturing</i>	<i>Battery assembly</i>	<i>Fixed CNT, semiconductor-CNT composites, functionalised MWCNT or SWCNT</i>	<i>Occupational</i>	<i>D3</i>
Process steps in battery assembly include electrode insertion into battery casing and case welding. Free CNTs are not anticipated to be released under such normal process situations. Once the battery has been sealed with plastic wrap, CNTs are not anticipated to be released under normal product use. However, no public domain data is available currently on the potential release of CNT from such situations.				
<i>Manufacturing</i>	<i>Equipment maintenance</i>	<i>Free or fixed CNT, semiconductor-CNT composites, functionalised MWCNT or SWCNT</i>	<i>Occupational</i>	<i>B3</i>
It is anticipated that maintenance of equipment for CNT-containing pre-cursors may generate particulate emissions of CNTs, CNT-composites, or their aggregates, and be a secondary sources of aerosolisable CNT-containing material from residual material. Factors that can be expected to influence the potential for release and inhalation exposure to CNT include the physical state of the CNT material used (e.g. powder, dispersion, pre-mixed batches), the quantity of residual material to be removed, the anticipated dustiness of the cleaning and maintenance processes, and the effectiveness of containment and particulate control measures in place (e.g. ventilated enclosures or LEV). Whilst there is no published evidence of release in this specific scenario, as previously mentioned, agitation and aerosolisation of CNT from mixing tasks have demonstrated the release potential of CNT (e.g. Maynard et al 2004, Han et al 2008).				
<i>Manufacturing</i>	<i>Accidents</i>	<i>Free or fixed CNT, semiconductor-CNT composites, functionalised MWCNT or SWCNT</i>	<i>Occupational</i>	<i>B3</i>
It is anticipated that accidents involving CNT-containing pre-cursors, prior to encapsulation, may generate particulate emissions of CNTs, CNT-composites, or their aggregates, leading to secondary sources of aerosolisable CNT-containing material from dried spilled or residual material. No public domain data is available currently on the potential release of CNT from such situations.				

Activity Class	Activity	Material	Exposure group	Exposure ranking
<i>Transport</i>	<i>Routine transport of manufactured batteries</i>	<i>Fixed CNT, semiconductor-CNT composites, functionalised MWCNT or SWCNT</i>	<i>Occupational, Environmental</i>	<i>D3</i>
Release and inhalation exposure is not anticipated under normal transportation circumstances.				
<i>Transport</i>	<i>Accidents</i>	<i>Fixed CNT, semiconductor-CNT composites, functionalised MWCNT or SWCNT</i>	<i>Occupational, Environmental</i>	<i>C3</i>
The effects of a substantial mechanical force causing damage, exposure to high temperature, and chemical incompatibilities causing corrosion of the casing material and a containment failure are the principle factors to consider in the assessment of the potential for exposure from accidents. Such situations might only be anticipated to have the potential to release measurable CNTs when large quantities of batteries are involved, such as in storage. However, no public domain data is available currently on the potential release of CNT from such situations.				

Activity Class	Activity	Material	Exposure group	Exposure ranking
<i>Use</i>	<i>Routine use</i>	<i>Fixed CNT, semiconductor-CNT composites, functionalised MWCNT or SWCNT</i>	<i>Consumer, Occupational</i>	<i>D3</i>
Once the battery has been sealed with plastic wrap, CNTs are not anticipated to be released under normal product use. However, no public domain data is available currently on the potential release of CNT from such situations.				
<i>Use</i>	<i>Accidents</i>	<i>Fixed CNT, semiconductor-CNT composites, functionalised MWCNT or SWCNT</i>	<i>Consumer Occupational</i>	<i>C3</i>
Possible accident scenarios associated with normal use of Li-ion sec batteries containing CNT include inappropriate charging, exposure to high temperature and mechanical force causing damage. Whilst it is not anticipated that such accidents would generate measurable particulate emissions of CNTs, CNT-composites, or their aggregates, no public domain data is available currently on the potential release of CNT from such situations.				

Activity Class	Activity	Material	Exposure group	Exposure ranking
<i>Disposal</i>	<i>Waste collection</i>	<i>Fixed CNT, semiconductor-CNT composites, functionalised MWCNT or SWCNT</i>	<i>Occupational, Environmental</i>	<i>D3</i>
Waste collection and separation are not expected to cause damage leading to measurable release and inhalation exposure under normal circumstances. Whilst compaction of batteries inappropriately disposed of in domestic waste may cause damage to the casing, but this is not expected to result in measurable release and inhalation exposure, no public domain data is available currently on the potential release of CNT from such situations.				
<i>Disposal</i>	<i>Incineration (controlled conditions)</i>	<i>Fixed CNT, semiconductor-CNT composites, functionalised MWCNT or SWCNT</i>	<i>Occupational, Environmental</i>	<i>B3</i>
Free SWCNT ignite in the presence of oxygen at approximately 600°C. Therefore, the controlled conditions of industrial waste incineration process (temperatures >850°C, and retention times of up to 60 minutes) are likely to destroy CNT materials, except perhaps the densely packed CNT inside the metallic casing as there it may not be exposed to oxygen during incineration. It is also known that under reductive conditions, SWCNT start transforming at around 1200°C and may reform into MWCNT at around 2200°C. Therefore cylindrical cells, which enter the slag, can still contain CNT.				
<i>Disposal</i>	<i>Incineration (uncontrolled conditions)</i>	<i>Fixed CNT, semiconductor-CNT composites, functionalised MWCNT or SWCNT</i>	<i>Occupational, Environmental</i>	<i>B3</i>

Uncontrolled incineration, for example in uncontrolled fires, is unlikely to incinerate the CNT and so may present a greater risk of potential exposure.				
Disposal	Landfill	<i>Fixed CNT, semiconductor-CNT composites, functionalised MWCNT or SWCNT</i>	<i>Occupational, Environmental</i>	<i>D3</i>
Batteries disposed to landfill are likely to corrode over time, however, it is not known whether CNTs will be available to migrate into soil/ water environments from the electrode material. The likelihood of significant quantities of CNT-containing material in landfill presenting an inhalation exposure potential is considered to be low, although there is no information in the public domain to evaluate the extent and significance of this as a source of potential CNT exposure via the environment.				

Activity Class	Activity	Material	Exposure group	Exposure ranking
<i>Recycling</i>	<i>Processing</i>	<i>Fixed CNT, semiconductor-CNT composites, functionalised MWCNT or SWCNT</i>	<i>Occupational, Environmental</i>	<i>B2</i>
It is anticipated that processes involving the recycling of CNT-containing Li-ion sec batteries, including manual dismantling, mechanical shredding and/or milling, mechanical sorting (such as by sieving or application of magnetic field), and thermal processing (such as pyrolysis and smelting) may generate particulate emissions of CNTs, CNT-composites, or their aggregates. Any waste gas treatment control measures used in automated battery recycling facilities may be sufficient to prevent exposure. Manual processing has the potential for release of CNTs into the occupational settings and exposure of the workforce. Thermal processing of batteries does not eliminate CNTs; as they are reported to be transferred into granulate interstage products (e.g. cobalt fraction). These granulate materials have been considered a major source of CNT-emission because their handling would take place outside controlled environments. Factors that can be expected to influence the potential for release and inhalation exposure to CNT include the physical state of the CNT material as-supplied, quantities to be handled, anticipated dustiness of the processes, process containment and particulate control measures in place (e.g. ventilated enclosures or LEV). No public domain data is available currently on the potential release of CNT from such situations.				

5.2.2 Carbon Nanotubes in Epoxy Resins and Nanocomposites

Activity Class	Activity	Material	Exposure group	Exposure ranking
<i>Manufacturing</i>	<i>Pre-cursor preparation</i>	<i>Free or fixed CNT / functionalised MWCNT or SWCNT</i>	<i>Occupational</i>	<i>B1</i>
<p>It is anticipated that processes involving CNT prior to their dispersion in solvents or polymer melts may generate particulate emissions of CNTs or their aggregates. These include powder handling (decanting and weighing), blending and disposal of waste materials. Factors that can be expected to influence the potential for release and inhalation exposure to CNT include the physical state of the CNT material as-supplied (e.g. powder, dispersion, pre-mixed batches*), quantities to be handled, anticipated dustiness of the blending process, containment and particulate control measures in place (e.g. ventilated enclosures or LEV). Mixing tasks have demonstrated release potential of CNT (e.g. Maynard et al 2004, Han et al 2008, Methner et al 2006 & 2007, Bello et al 2008) and the industrial risk assessment for the incorporation of single and multi-walled CNT into polymer nanocomposites (DuPont 2007) is available as evidence of the potential for release of CNT from such situations.</p> <p>*Use of pre-prepared masterbatches containing blended CNT absolves the user of the need to handle powder CNT and therefore presents a lower potential for release and inhalation exposure (although clearly a risk remains with the preparation of the masterbatch). Nanotube concentrations in polymer masterbatches will depend on the intended application; concentrations can range from as low as 0.002% w/w for improved electrical properties to ~60% w/w for reinforcement applications. Masterbatches for use by composite manufacturers (who then further dilute the masterbatch in co-polymer to the concentrations required) containing CNT for anti-static properties, have ~7% w/w of CNT.</p>				
<i>Manufacturing</i>	<i>Polymer compounding</i>	<i>Free or fixed CNT/r functionalised MWCNT or SWCNT</i>	<i>Occupational</i>	<i>B1</i>
<p>It is anticipated that some steps in polymer compounding processes may generate particulate emissions of CNTs or their aggregates. These include transfer of pre-cursor materials containing CNTs to moulding machines, batch mixing, extrusion, removal of CNT-containing polymeric material, and cutting / shaping. Further compounding, machining, surface-finishing, grinding, and handling of defective or off-quality parts may also be anticipated to the potential to generate particulate emissions of CNTs, CNT-composites or their aggregates. Mixing and machining tasks have demonstrated release potential of CNT (e.g. Maynard et al 2004, Han et al 2008, Methner et al 2006 & 2007, Bello et al 2008) and the industrial risk assessment for the incorporation of single and multi-walled CNT into polymer nanocomposites (DuPont 2007) is available as evidence of the potential for release of CNT from such situations. Factors that can be expected to influence the potential for release and inhalation exposure to CNT include the physical state of the CNT material used in the pre-cursor material (e.g. powder, dispersion, pre-mixed batches), quantities to be handled, anticipated dustiness of the blending process, containment and particulate control measures in place (e.g. ventilated enclosures or LEV). Measurable quantities of CNTs are not anticipated to be released under normal handling of finished nanocomposites.</p>				
<i>Manufacturing</i>	<i>Resin curing</i>	<i>Fixed CNT / functionalised MWCNT or SWCNT</i>	<i>Occupational</i>	<i>C3</i>
<p>Release and inhalation exposure is not anticipated under normal circumstances. However, it may be possible, although unlikely, for run-away cure reactions to char and decompose the resin system, generating vapours and particulates which may contain CNT, although no data available on the release of CNT from such reactions.</p>				
<i>Manufacturing</i>	<i>Equipment maintenance</i>	<i>Free or fixed CNT / functionalised MWCNT or SWCNT</i>	<i>Occupational</i>	<i>B3</i>
<p>It is anticipated that maintenance of equipment for CNT-containing pre-cursors may generate particulate emissions of CNTs, CNT-composites, or their aggregates, and be a secondary sources if CNT-containing material from residual material can be aerosolised. Factors that can be expected to influence the potential for release and inhalation exposure to CNT include the physical state of the CNT material used (e.g. powder, dispersion, pre-mixed batches), quantity of residual material to be removed, anticipated dustiness of the cleaning and maintenance processes, containment and particulate control measures in place (e.g. ventilated enclosures or LEV). No public domain data is available currently on the potential release of CNT from such situations.</p>				
<i>Manufacturing</i>	<i>Waste materials</i>	<i>Free or fixed CNT / functionalised MWCNT or SWCNT</i>	<i>Occupational</i>	<i>B3</i>
<p>It can be anticipated that only waste CNT not incorporated into epoxy, dispersions or solvents may present a potential inhalation exposure hazard. Similar to the consideration of equipment maintenance, it is anticipated that waste CNT-containing pre-cursors may generate particulate emissions of CNTs, CNT-composites, or their aggregates, and be secondary sources if CNT-containing material from residual material can be aerosolised. Disposal of unused pre-hardened epoxy in liquid form is addressed under Disposal below.</p>				
<i>Manufacturing</i>	<i>Accidents</i>	<i>Free or fixed CNT or functionalised MWCNT or SWCNT</i>	<i>Occupational</i>	<i>B3</i>

It is anticipated that accidents involving CNT-containing resins and composites may generate particulate emissions of CNTs, CNT-composites, or their aggregates, leading to secondary sources of aerosolisable CNT-containing material from dried spilled or residual material. Potential chemical incompatibilities should also be considered: whilst CNT-containing concentrates are stable at room temperature, they can potentially react vigorously with strong oxidising agents, strong Lewis or mineral acids, and strong mineral and organic bases, especially primary and secondary aliphatic amines. No public domain data is available currently on the potential release of CNT from such situations.

Activity Class	Activity	Material	Exposure group	Exposure ranking
<i>Transport</i>	<i>Routine transport of materials</i>	<i>Fixed CNT / functionalised MWCNT or SWCNT</i>	<i>Occupational, Environmental</i>	<i>D3</i>
Release and inhalation exposure is not anticipated under normal transportation circumstances.				
<i>Transport</i>	<i>Accidents</i>	<i>Fixed CNT / functionalised MWCNT or SWCNT</i>	<i>Occupational, Environmental</i>	<i>C3</i>
The effects of exposure to high temperature and chemical incompatibilities are the principle factors to consider in the assessment of the potential for exposure from accidents. Such situations might only be anticipated to have the potential to release measurable CNTs when large quantities of the resin or nanocomposite are involved, such as in storage. However, no public domain data is available currently on the potential release of CNT from such situations.				

Activity Class	Activity	Material	Exposure group	Exposure ranking
<i>Use</i>	<i>Routine handling of liquid epoxy</i>	<i>Fixed CNT / functionalised MWCNT or SWCNT</i>	<i>Occupational, Consumer</i>	<i>D3</i>
<p>Typical quantities of liquid-based epoxy resin available to consumers range from small tubes containing a few millilitres to larger containers holding of the order of 40kg. However, for the larger volume containers which cannot prevent significant amounts of the material being exposed to the atmosphere once opened, the lifetime of an opened container is of the order of an hour or less, after which the epoxy begins to harden and is no longer usable.</p> <p>CNTs are not anticipated to be released under normal handling of epoxy solutions, putty, fabric patches, and subsequent use of hardened epoxy and nanocomposites in articles.</p>				
<i>Use</i>	<i>Machining manufactured product</i>	<i>Fixed CNT / functionalised MWCNT or SWCNT</i>	<i>Occupational, Consumer</i>	<i>C3</i>
<p>Further compounding, machining, surface-finishing and grinding may be anticipated to generate particulate emissions containing CNTs, CNT-composites or their aggregates. Physical disturbance of CNT-containing composite may generate particulate emissions, although the potential for release of airborne CNTs will depend on the strength of the binding within the polymer matrix. Machining tasks have demonstrated release potential of CNT (e.g. Methner et al 2006 & 2007, Bello et al 2008). Factors that can be expected to influence the potential for release and inhalation exposure to CNT include the quantities of CNT-containing materials being handled, anticipated dustiness of the process, containment and particulate control measures in place (e.g. ventilated enclosures or LEV).</p>				
<i>Use</i>	<i>Accidents</i>	<i>Fixed CNT / functionalised MWCNT or SWCNT</i>	<i>Occupational, Consumer</i>	<i>C3</i>
<p>Possible accident scenarios associated with normal use of nanocomposites and resins containing CNT include exposure to high temperature and mechanical force causing damage. Free SWCNT ignite in the presence of oxygen at approximately 600°C, but retention times of up to 60 minutes as with incineration are needed to destroy CNT materials. Although it is not anticipated that such accidents would generate measurable particulate emissions of CNTs, CNT-composites, or their aggregates, no public domain data is available currently on the potential release of CNT from such situations.</p>				

Activity Class	Activity	Material	Exposure group	Exposure ranking
<i>Disposal</i>	<i>Waste collection</i>	<i>Fixed CNT / functionalised MWCNT or SWCNT</i>	<i>Occupational, Environmental</i>	<i>D3</i>
<p>Realistically, small volumes of unused pre-hardened epoxy still in liquid form may be expected in refuse. However, the epoxy is supplied in a robust container, which may be expected to prevent release of the liquid material. If liquid material were to be released caused a failure of the container during compaction of waste, hardening will start to take place. The likelihood of significant quantities of CNT-containing liquid epoxy existing in the environment is considered low, although there is no information in the public domain to evaluate the extent and significance of this as a source of potential CNT exposure via the environment.</p> <p>Waste collection and separation of hardened epoxy or nanocomposites are not expected to cause damage leading to measurable release and inhalation exposure under normal circumstances. Whilst compaction may cause damage to the composites and resins, this is not expected to result in measurable release and inhalation exposure, no public domain data is available currently on the potential release of CNT from such situations.</p>				
<i>Disposal</i>	<i>Incineration</i>	<i>Fixed CNT / functionalised MWCNT or SWCNT</i>	<i>Occupational, Environmental</i>	<i>C3</i>
<p>Free SWCNT ignite in the presence of oxygen at approximately 600°C. Therefore, incineration process (temperatures >850°C, and retention times of up to 60 minutes) is likely to destroy CNT materials, except where the composite material is fire resistant, preventing the CNTs being exposed to oxygen during incineration. It is also known that under reductive conditions, SWCNT start transforming at around 1200°C and may reform into MWCNT at around 2200°C.</p>				
<i>Disposal</i>	<i>Incineration (uncontrolled conditions)</i>	<i>Fixed CNT / functionalised MWCNT or SWCNT</i>	<i>Occupational, Environmental</i>	<i>B3</i>
<p>Uncontrolled incineration, for example in uncontrolled fires, is unlikely to incinerate the CNT and so may present a greater risk of potential exposure.</p>				
<i>Disposal</i>	<i>Landfill</i>	<i>Fixed CNT / functionalised MWCNT or SWCNT</i>	<i>Occupational, Environmental</i>	<i>D3</i>
<p>Typical quantities of liquid-based epoxy resin available to consumers range from small tubes containing a few millilitres to larger containers holding of the order of 40kg. However, for the larger volume containers which cannot prevent significant amounts of the material being exposed to the atmosphere once opened, the lifetime of an opened container is of the order of an hour or less, after which the epoxy begins to harden and is no longer usable. Disposal of unused pre-hardened epoxy still in liquid form by consumers may be expected for small volumes and present a potential source of CNT-containing material. However, the epoxy is supplied in a robust container, which will take some time to break down, which would then allow air to act on the epoxy and hardened the material. The likelihood of significant quantities of CNT-containing liquid epoxy existing in the environment is considered low, although there is no information in the public domain to evaluate the extent and significance of this as a source of potential CNT exposure. Nanocomposites and resins disposed of to landfill are likely to degrade over time, but again it is not known whether CNTs can be released from the hardened material and migrate into soil/ water environments.</p>				

Activity Class	Activity	Material	Exposure group	Exposure ranking
<i>Recycling</i>	<i>Processing</i>	<i>Fixed CNT / functionalised MWCNT or SWCNT</i>	<i>Occupational, Environmental</i>	<i>B2</i>
<p>It is anticipated that processes involving the recycling of CNT-containing nanocomposites and resins, including separating, chemically cleaning, grinding, chopping, milling, re-melting, mixing, re-pelletising, and re-compounding may generate particulate emissions containing CNTs, CNT-composites, or their aggregates. Manual processing has the potential for release of CNTs into the occupational settings and exposure of the workforce. Factors that can be expected to influence the potential for release and inhalation exposure to CNT include the physical state of the materials for recycling, quantities to be handled, anticipated dustiness of the processes, process containment and particulate control measures in place (e.g. ventilated enclosures or LEV). No public domain data is available currently on the potential release of CNT from such situations.</p>				

5.2.3 Carbon Nanotubes in Textiles: CNT incorporated into yarn

Activity Class	Activity	Material	Exposure group	Exposure ranking
<i>Manufacturing</i>	<i>Handling, mixing prior to spinning</i>	<i>CNT</i>	<i>Occupational</i>	<i>B1</i>
<p>This task would include handling of the CNT as delivered from the suppliers and preparation of same for incorporation into the process. It could include bag opening, scooping, weighing. This may be automated or manual. Mixing tasks would include loading into the reactor or container followed by the mixing process, usually with some mechanical activity. The mixing chamber may be open or closed. Mixing may occur at the nozzle although it is not clear whether this is used in CNT processes. Exposure would vary dependant on the nature of the CNTs as delivered, (e.g. dry, in suspension or in a masterbatch), the level of automation and the effectiveness of control measures used. There is no published evidence of release in this specific setting (i.e. in textile area) on which to assess exposure.</p> <p>However handling and mixing of CNT in other settings have demonstrated that there is release potential (Maynard <i>et al</i> 2004, Han <i>et al</i> 2008, Methner <i>et al</i> 2006, 2007), particularly if control approaches are not implemented effectively.</p> <p>Han <i>et al</i> monitored the possible exposure to MWCNT release in a carbon nanotube research laboratory (i.e. not at an industrial scale). In a range of activities including blending (mixing). Mass concentrations of up to 0.43 mg.m⁻³ were reported during blending before exposure control was implemented. Following implementation of exposure control (hood and ventilation), the maximum measured concentration (mass) was 0.04 mg.m⁻³. The fibres were only found in the blending scenario and were found on both personal and area samples at approximately the same level. The reported number concentration was very high (193.6 and 172.9 fibre ml⁻¹). For reference, these are two orders of magnitude greater than typical asbestos workplace exposure limits of 0.1 fibre ml⁻¹ against which it may be reasonable to compare CNT.</p> <p>The study carried out by Maynard <i>et al</i> in 2004 focussed mainly activities concerning the synthesis and recovery of SWCNT. In simulated handling activities they measured concentrations up to 53 □g m⁻³.</p> <p>One factor to consider is the proportion of CNT which is likely to be used. At this stage of development, prior to full production, this is still the subject of research to find appropriate combinations. This was reviewed by Kohler <i>et al</i> (2008) who identified data for a range of matrix polymers including polyacrylonitrile, polypropylene, polyethylene and polyester. CNT weight percentage ranged from 1 to 20%.</p> <p>It is very difficult to judge the extent to which the conditions in these studies, all at a laboratory scale are representative of likely condition in commercial scale activities. However, measurable concentration in similar activities highlights the need for more data to be collected.</p>				
<i>Manufacturing</i>	<i>Spinning</i>	<i>CNT / polymer matrix</i>	<i>Occupational</i>	<i>C2</i>
<p>Synthetic yarns are generally produced in hot processes. Polymer chips are melted at temperatures of around 270°C. The molten polymer is then extruded through a spinneret and the filaments are subsequently drawn into the desired polyester fibre. Mixing may occur dynamically at or near the nozzle. After extrusion from the spinneret, the fibres are drawn or elongated. Yarns can be monofilament or multifilament by twisting several together. Depending upon the desired properties, the polyester fibres are usually drawn up to five times its original length. For higher tenacity, the filaments are drawn to a greater extent. When the fibres come in contact with the air, they solidify. After the polyester yarn is drawn, it is wound on large bobbins or flat-wound packages, ready to be woven into material. In spinning there will be mechanical contact between the yarns and with the formers with the yarn moving at high speed. This high energy activity may lead to shedding of fibres. If fibres are shed, they are more likely to be they are more likely to be of the composite (i.e. polymer and CNT combined) than CNT alone.</p> <p>We have no exposure data available for this process with CNT. Kohler <i>et al</i> (2008) commented that “textile experts do not expect considerable particle release during spinning and weaving”. However exposures in the production of other synthetic fibres have been observed. Cherrie <i>et al</i> 1995 measured fibre dust exposure during para-aramid manufacturing their 8-hour time-weighted average exposure to respirable fibrils. Geometric mean concentrations for different jobs were generally low, ranging from 0.005 to 0.4 fibres ml⁻¹. Assuming a log-normal distribution, less than 1% of the exposure levels would be expected to exceed 0.5 fibres ml⁻¹ and about 0.002% would be above 2 fibres ml⁻¹. This work suggests that exposures during this activity are plausible.</p>				
<i>Manufacturing</i>	<i>Weaving</i>	<i>CNT / polymer matrix</i>	<i>Occupational</i>	<i>C2</i>
<p>In weaving there will be mechanical contact between yarns and between the yarns and with the formers. This may lead to shedding of fibres. No CNT exposure data is available for this process. However the work of Cherrie <i>et al</i> (1995) on exposures during production of para-aramid suggests that as in spinning exposures during this activity are plausible. Levels are likely to be similar to spinning.</p>				

Activity Class	Activity	Material	Exposure group	Exposure ranking
Manufacturing	Finishing	CNT / polymer matrix	Occupational	D3
Finishing could include, inspection, cleaning, washing and packing. It may be manual or automated. No CNT exposure data is available for this process. Finishing is likely to be a lower energy process than spinning or weaving and so the probability of fibre release is lower.				
Manufacturing	Accidents - spillage	CNT, CNT / polymer matrix	Occupational	B3
This could include spillage of CNT or CNT formulation, contamination of the workplaces and exposure during subsequent cleanup. In many industrial processes clean up after spillage is a major source of exposure. Again we have no direct data from the manufacture or use of synthetic textile containing CNT.				
Manufacturing	Accidents - fire	CNT / CNT / ash mix	Occupational, Environmental	B1
Major accidents, such as a fire in a storage facility may create the potential for release into the environment and the potential for occupational exposure to those attending the fire or involved in the clean up after it. It is expected that in controlled incineration (see disposal) of composites will result in complete incineration of CNT. It has been shown that CNT (MWCNT and SWCNT) will burn of completely at 740°C (Wang et al 2006). However, incineration at lowered temperatures will not necessarily result in destruction of the CNT (Kashiwagi et al 2002). This could result in the formation of ash containing CNT at elevated levels. No data available from accidental incineration of CNT polymers.				

Activity Class	Activity	Material	Exposure group	Exposure ranking
Transport	Transport of finished item	CNT, CNT / polymer matrix	Occupational	D3
Exposure is likely to be small, as garments are likely to be packed or otherwise enclosed.				
Transport	Accidents	CNT, CNT / polymer matrix	Occupational, Environmental	B1
The main danger from accident would be exposure to high temperature in the event of a fire (see manufacturing, accidents – fire).				

Activity Class	Activity	Material	Exposure group	Exposure ranking
Use	Wearing	CNT, CNT / polymer matrix	Consumer	D2
<p>During use garments typically suffer a 10% weight loss (Kohler et al 2008) although this must be highly dependent on the specific type of material. One of the reasons for using synthetic materials is that they are considered to be “hard wearing”. Various processes contribute to this including mechanical abrasion, thermal degradation, photo-oxidative degradation and weathering. It is likely that most of the weight loss would occur during the washing process.</p> <p>However, wearing may cause polymer fibres containing to be shed. Shedding of fibres would not necessarily be expected to become airborne, rather might be expected that they would transfer to the skin on to other clothing and be subsequently washed off. Synthetic materials of this type would normally be considered hard wearing, and addition of CNT would be anticipated to enhance this property, further reducing the likelihood of inhalation exposure.</p> <p>If there is shedding, this could present a chronic low level exposure to the wearer, to those in contact with the wearer (family and children) and to the wearers in home environment. No information on this process is available for CNT polymers but it is anticipated to be low. The following example, although not entirely trivial, is likely to be a worst case and is calculated with many assumptions:</p> <p>Typical weight of a T-shirt - 250 g Assume wearer owns 4 such items – 1000g Incorporation of CNT at a 10% weight ratio – 100g of CNT During use, over 3 years, the garment loses 10% - 10g of CNT Most of this would be in washing lets assume 10% would be in wearing stage – 1 g of CNT Only a small proportion of this could become airborne, assume 10% - 0.1 g of CNT Assume loss to be linear over 3 years (1000 days), the amount becoming airborne per day would be - 0.0001g Assume that this would be dispersed into 1000m³ of air, this would result in a concentration of 0.000001gm⁻³ = 1 □ gm⁻³</p>				
Use	Washing	CNT / polymer matrix	Occupational, Consumer	D3

<p>Washing may cause fibres to be released but any fibres released are likely to be retained within the waste water and so will not provide an inhalation exposure. Overtime there may be some build up of released fibres on filters or otherwise within the machine but again this would be unlikely to inhalation exposure, even during cleaning. Tumble drying may provide enhanced shedding of fibres due to heating and drying. As above a failure to shed fibres would be considered an advantageous property. No information concerning exposure during these laundry processes is available for CNT polymer materials.</p>				
<i>Use</i>	<i>Ironing</i>	<i>CNT / polymer matrix</i>	<i>Occupational, Consumer</i>	<i>D3</i>
<p>It is not expected that normal ironing would result in fibre release.</p>				
<i>Use</i>	<i>Accident – exposure to high temperature</i>	<i>CNT, CNT / polymer matrix</i>	<i>Consumer</i>	<i>B1</i>
<p>Ironing may cause thermal decomposition of burning of the material. Accidental burning in the home is also plausible. Synthetic textiles disintegrate at temperatures of more than 200°C (Kohler 2008). Incineration at these temperatures leaves an ash cake which contains CNT (Kashiwagi, 2008). It is not known if CNT would enter the smoke emitted from this event. No information of release of CNT into the air as a result of this process is available.</p>				

Activity Class	Activity	Material	Exposure group	Exposure ranking
<i>Disposal</i>	<i>Landfill</i>	<i>CNT / polymer matrix</i>	<i>Occupational, Environmental</i>	<i>D3</i>
<p>The land filing process could involve mechanical processes which could cause release to the air and exposure of the workers involved in that activity. No information is available on exposure from this process. Once landfill has been complete release to the air is unlikely.</p>				
<i>Disposal</i>	<i>Incineration - controlled</i>	<i>CNT / polymer matrix</i>	<i>Occupational, Environmental</i>	<i>D3</i>
<p>Controlled incineration of textiles, (such as in municipal incinerators) will almost certainly incinerate the CNT due to the elevated temperatures involved (>800°C). These systems also include filtration of the flue gasses so any CNT release would be capture.</p>				
<i>Disposal</i>	<i>Incineration (uncontrolled)</i>	<i>CNT / polymer matrix</i>	<i>Occupational, Environmental</i>	<i>B2</i>
<p>Uncontrolled incineration, for example in uncontrolled fires, is unlikely to incinerate the CNT and so may present a greater risk of exposure. Synthetic textiles disintegrate at temperatures of more than 200°C (Kohler 2008). Incineration at these temperatures leaves an ash cake which contains CNT (Kashiwagi, 2008). It is not known if CNT would enter the smoke emitted from this event. No information of release of CNT into the air as a result of this process is available.</p>				
<i>Disposal</i>	<i>Shredding / milling / recycling</i>	<i>CNT / polymer matrix</i>	<i>Occupational, Environmental</i>	<i>D2</i>
<p>Textiles undergo various types of mechanical, thermal and chemical treatment as part of the recycling process. All of these could potentially lead to exposure.</p>				
<i>Disposal</i>	<i>Recycling</i>	<i>CNT / polymer matrix</i>	<i>Occupational, Environmental</i>	<i>C2</i>
<p>Textiles undergo various types of mechanical, thermal and chemical treatment as part of the recycling process. All of these could potentially lead to exposure.</p>				

5.2.4 Carbon Nanotubes in Textiles: CNT applied as a coating

Activity Class	Activity	Material	Exposure group	Exposure ranking
<i>Manufacturing</i>	<i>Handling / mixing</i>	<i>CNT</i>	<i>Occupational</i>	<i>B1</i>
<p>Activities would include handling of the CNT as delivered from the suppliers and preparation of same for incorporation into the process. It could include bag opening, scooping, weighing. This may be automated or manual. Exposure would vary dependant on the nature of the CNTs as delivered, (e.g. dry, in suspension or in a masterbatch), the level of automation and the effectiveness of control measures used.</p> <p>No published evidence of release in the this specific scenario (i.e. in textile area) however handling tasks in other settings have demonstrated release potential (e.g. Maynard et al 2004, Han et al 2008, Methner et al 2006, 2007).</p>				
<i>Manufacturing</i>	<i>Coating</i>	<i>CNT, CNT / solvents</i>	<i>Occupational</i>	<i>A3</i>
<p>Possible spraying or dipping activity using a suspension of CNTs. Coating could be applied to the yarn or to finished textiles or garments. Most published work currently describes coating by submersion in a bath. For example Xue et al 2007 describes coating of a range of fibre types with CNT to create a conductive fibre by drawing them through a coagulation bath containing a gel.</p> <p>However spray coating is a common process with finished textiles e.g. for the purpose of waterproofing. We have not yet been able to find any evidence of this process being applied using nanotubes. Any spraying activity clearly has the potential for exposure if not carried out under suitably controlled condition. If a spray coating method was used then a significant potential for inhalation exposure exists, if the process is not controlled adequately.</p>				
<i>Manufacturing</i>	<i>Weaving</i>	<i>CNT</i>	<i>Occupational</i>	<i>B2</i>
<p>In weaving there will be mechanical contact between yarns and between the yarns and with the formers. This may lead to shedding of fibres. The CNTs reside on the surface then the likelihood is that it is these which will be shed first. No CNT exposure data is available for this process. However the work of Cherrie et al (1995) on exposures during production of para-aramid suggests that as in spinning exposures during this activity are plausible. Levels are likely to be similar to spinning.</p>				
<i>Manufacturing</i>	<i>Finishing</i>	<i>CNT, CNT / binder</i>	<i>Occupational</i>	<i>B2</i>
<p>Finishing could include, inspection, cleaning, washing and packing. It may be manual or automated. No CNT exposure data is available for this process. Finishing is likely to be a lower energy process than spinning or weaving and so the probability of fibre release is lower.</p>				
<i>Manufacturing</i>	<i>Accidents - spillage</i>	<i>CNT</i>	<i>Occupational</i>	<i>B3</i>
<p>This could include spillage of CNT or CNT formulation, contamination of the workplaces and exposure during subsequent clean up. In many industrial processes clean up after spillage is a major source of exposure. Again we have no direct data from the manufacture or use of synthetic textile containing CNT.</p>				
<i>Manufacturing</i>	<i>Accidents - fire</i>	<i>CNT, CNT / ash mix</i>	<i>Occupational, Environmental</i>	<i>B1</i>
<p>Major accidents, such as a fire in a storage facility may create the potential for release into the environment and the potential for occupational exposure to those attending the fire or involved in the clean up after it. It is expected that in controlled incineration (see disposal) of composites will result in complete incineration of CNT. It has been shown that CNT (MWCNT and SWCNT) will burn of completely at 740°C (Yang et al 2004). However, incineration at lowered temperatures will not necessarily result in destruction of the CNT (Kashiwagi et al 2002). This could result in the formation of ash containing CNT at elevated levels. No data available from accidental incineration of CNT polymers</p>				

Activity Class	Activity	Material	Exposure group	Exposure ranking
<i>Transport</i>	<i>Transport of finished item</i>	<i>CNT, CNT binder</i>	<i>Occupational</i>	<i>D3</i>
Exposure is likely to be small, as garments are likely to be packed or otherwise enclosed.				
<i>Transport</i>	<i>Accidents</i>	<i>CNT, CNT / polymer matrix</i>	<i>Occupational, Environmental</i>	<i>B1</i>
The main danger from accidents would be exposure to high temperature in the event of a fire (see manufacturing, accidents – fire).				

Activity Class	Activity	Material	Exposure group	Exposure ranking
<i>Use</i>	<i>Wearing</i>	<i>CNT, CNT / polymer matrix</i>	<i>Consumer</i>	<i>B2</i>
<p>As described above, during use garments typically suffer a 10% weight loss (Kohler et al 2008) although this must be highly dependent on the specific type of material. On of the reasons for using synthetic materials is that they are considered to be “hard wearing”. Various processes contribute to this including mechanical abrasion, thermal degradation, photo-oxidative degradation and weathering. It is likely that most of the weight loss would occur during the washing process. There would be additional concerns if the CNT were on the outside of the fibres.</p> <p>However, wearing may cause polymer fibres containing to be shed. Shedding of fibres would not necessarily be expected to become airborne, rather might be expected that they would transfer to the skin on to other clothing and be subsequently washed off. Synthetic materials of this type would normally be considered hard wearing, and addition of CNT would be anticipated to enhance this property, further reducing the likelihood of inhalation exposure.</p> <p>If there is shedding, this could present a chronic low level exposure to the wearer, to those in contact with the wearer (family and children) and to the wearers in home environment. No information on this process is available for these types of textiles.</p>				
<i>Use</i>	<i>Washing</i>	<i>CNT / polymer matrix</i>	<i>Occupational, Consumer</i>	<i>D3</i>
Washing may cause fibres to be released but any fibres released are likely to be retained within the waste water and so will not provide an inhalation exposure. Overtime there may be some build up of released fibres on filters or otherwise within the machine but again this would be unlikely to inhalation exposure, even during cleaning. Tumble drying may provide enhanced shedding of fibres due to heating and drying. As above a failure to shed fibres would be considered an advantageous property. No information concerning exposure during these laundry processes is available for CNT polymer materials.				
<i>Use</i>	<i>Ironing</i>	<i>CNT / polymer matrix</i>	<i>Occupational, Consumer</i>	<i>D3</i>
It is not expected that normal ironing would result in fibre release.				
<i>Use</i>	<i>Accident – exposure to high temperature</i>	<i>CNT, CNT / polymer matrix</i>	<i>Consumer</i>	<i>B1</i>
Ironing may cause thermal decomposition of burning of the material. Accidental burning in the home is also plausible. Synthetic textiles disintegrate at temperatures of more that 200° C (Kohler 2008). Incineration at these temperatures leaves an ash cake which contains CNT (Kashiwagi, 2008). It is not known if CNT would enter the smoke emitted from this event. No information of release of CNT into the air as a result of this process is available.				

Activity Class	Activity	Material	Exposure group	Exposure ranking
<i>Disposal</i>	<i>Landfill</i>	<i>CNT / polymer matrix</i>	<i>Occupational, Environmental</i>	<i>D3</i>
The land filling process could involve mechanical processes which could cause release to the air and exposure of the workers involved in that activity. No information is available on exposure from this process. Once landfill has been complete release to the air is unlikely.				
<i>Disposal</i>	<i>Incineration - controlled</i>	<i>CNT / polymer matrix</i>	<i>Occupational, Environmental</i>	<i>D3</i>
Controlled incineration of textiles, (such as in municipal incinerators) will almost certainly incinerate the CNT due to the elevated temperatures involved (>800°C). These systems also include filtration of the flue gasses so any CNT release would be capture.				
<i>Disposal</i>	<i>Incineration (uncontrolled)</i>	<i>CNT / polymer matrix</i>	<i>Occupational, Environmental</i>	<i>B2</i>
Uncontrolled incineration, for example in uncontrolled fires, is unlikely to incinerated the CNT and so may present a greater risk of exposure. Synthetic textiles disintegrate at temperatures of more that 200°C (Kohler 2008). Incineration at these temperatures leaves an ash cake which contains CNT (Kashiwagi, 2008). It is not known if CNT would enter the smoke emitted from this event. No information of release of CNT into the air as a result of this process is available.				
<i>Disposal</i>	<i>Shredding / milling / recycling</i>	<i>CNT / polymer matrix</i>	<i>Occupational, Environmental</i>	<i>B2</i>
Textiles undergo various types of mechanical, thermal and chemical treatment as part of the recycling process. All of these could potentially lead to exposure.				
<i>Disposal</i>	<i>Recycling</i>	<i>CNT / polymer matrix</i>	<i>Occupational, Environmental</i>	<i>B2</i>
Textiles undergo various types of mechanical, thermal and chemical treatment as part of the recycling process. All of these could potentially lead to exposure.				

5.2.5: Comparative Summary of Activities and Products in order of Exposure Ranking Categories

CNT in Li-ion Batteries

Rank	Activity Class - Activity
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B1	Manufacturing - Pre-cursor material preparation
B2	Recycling - Processing
B3	Manufacturing - Equipment maintenance
	Manufacturing - Accidents
	Disposal - Incineration (controlled conditions)
	Disposal - Incineration (uncontrolled conditions)
C3	Manufacturing - Electrode manufacturing prior to battery sealing
	Transport - Accidents
	Use - Accidents
D3	Manufacturing - Battery assembly
	Transport - Routine transport of manufactured batteries
	Use - Routine use
	Disposal - Waste collection
	Disposal - Landfill

CNT in Epoxy / Nanocomposites

Rank	Activity Class - Activity
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B1	Manufacturing - Pre-cursor preparation
	Manufacturing - Polymer compounding
B2	Recycling - Processing
B3	Manufacturing - Equipment maintenance
	Manufacturing - Waste materials
	Manufacturing - Accidents
	Disposal - Incineration (uncontrolled conditions)
C3	Manufacturing - Resin curing
	Transport - Accidents
	Use - Machining manufactured product
	Use - Accidents
D3	Disposal - Incineration
	Transport - Routine transport of materials
	Use - Routine handling of liquid epoxy
	Disposal - Waste collection
	Disposal - Landfill

CNT in Textiles

Rank	Activity Class - Activity	
	CNT incorporated into yarn	CNT applied as a coating

A3		Manufacturing - Coating
		Transport - Accidents - fire
B1	Manufacturing - Handling and mixing	
	Use - Accident – exposure to high temperature	
	Manufacturing - Accidents - fire	
	Transport - Accidents	
B2		Manufacturing - Weaving
		Manufacturing - Finishing
		Use - Wearing
		Disposal - Shredding / milling / recycling
	Disposal - Incineration - uncontrolled	
B3	Manufacturing - Accidents - spillages	
C2	Manufacturing - Spinning	
	Manufacturing - Weaving	
	Disposal - Shredding / milling / recycling	
D2	Use - Wearing	
D3	Manufacturing - Finishing	Manufacturing - Handling / mixing
	Transport - Transport of finished items	
	Use - Washing	
	Use - Ironing	
	Disposal - Landfill	
	Disposal - Incineration	

5.3 Conclusions

In this work, we have attempted to identify, and where possible characterise, the potential exposures across the life cycle for three products – Li-ion batteries, epoxy resin and textiles containing CNTs. The main problem that we faced was the paucity of data in all cases relating to the specific applications of CNT in the scenarios described. Where possible we have drawn analogous data available from other similar scenarios. We also note that in the scenarios described, there a large number of variables including, for example, the quantities of CNT and substrate used, the duration of activities, and control methods adopted, which make generalisation challenging. For this reason, we have restricted our appraisal to trying to identify and rank situations where there is the *potential* for exposure to occur. Whether exposure does or does or not occur will depend on the variables in the specific case. We have also tried, where possible, to describe the nature of the exposure (i.e. whether it is ‘free’ CNT material or CNT in combination with for example a polymer matrix).

In our ranking of the data, we make the following observations:

- Most of the scenarios where there is the highest potential for exposure are at the production end of the life cycle. They relate to relatively common industrial activities such as spraying, handling and mixing. There are already adequate control methods for these types of activities, which if implemented correctly, should be effective in limiting exposure of workers.
- In the case of CNT-containing batteries, the chances of inhalation exposure during use stage will only occur if the batteries are intentionally or accidentally cut open. The main likelihood of CNT exposure relates to accidental release (e.g. fire), and recycling and disposal stages. People likely to be at most risk of exposure will be those working at the recycling or waste disposal premises, or in the immediate vicinity.
- In the case of textiles, we considered it necessary to further divide this into two cases:
 1. For textiles where the CNT was incorporated into the yarn at the spinning stage;
 2. Where CNT was added to the outer surface of the yarn in a post-production coating process; reflecting the different exposure potential in these cases.
- In the second textiles case, the potential for exposure to CNT alone is much higher than in case 1, and this is the only case where significant consumer exposure seems plausible (see Appendix 3). Other lifecycle stages where there is a likelihood of exposure include recycling (shredding and milling of worn-out textiles), and disposal through incomplete incineration. People likely to be exposed in this case would again be those working at the recycling or waste disposal premises, or in the immediate vicinity.
- CNT-containing epoxy adhesive resins may carry a risk of inhalation exposure during use only if there are conditions that lead to formation of aerosols. The main likelihood of exposure will be during disposal through incomplete incineration. It is also of note that epoxy resins generally have a relatively short shelf life (9 months in the case of the study product). There is therefore a need for a mechanism for collection of the unused (unhardened, liquid) epoxy resin after sell-by date for appropriate and safe disposal.
- Common to all the three product types studied is the need for development of mechanisms for appropriate end-of-life treatments (e.g. separate collection of spent CNT-containing batteries, recycling of CNT-containing batteries and textiles under controlled conditions, and processes that ensure complete incineration of CNT in the disposed of products).

- Urgent research is needed to address the almost total lack of exposure data for CNT-containing consumer products, and the appropriateness of end-of-life treatments. The findings of such research should also enable the manufacturers to develop safer products through better product design which is aimed at minimising the likelihood of exposure to CNTs (and/ or other nanomaterials) during subsequent stages in the lifecycle.

It is of note that CNTs are likely to undergo various transformation during manufacturing, use and end-of-life treatment of the products. The health effects of potential exposure to the product-derived CNTs may be different from neat CNTs that are generally used in toxicological studies. Research is therefore also needed to characterise CNTs in consumer products to inform the risk assessment process.

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Appendix 1: The scope of Life cycle concepts and risk assessment methods

	Risk Assessment				Life cycle concepts			
	Toxicology Translocation	Ecotoxicology and environmental behaviour	Analytics, monitoring (incl. material science)	*Exposure - effect studies, biomonitoring (incl. occupational health)	Life cycle thinking, perspective	Foresight, Roadmapping, etc.	Material flow analysis	LCA
Methods provide information on:								
Future nanoapplication and –products					x	x		(x)
Mode of ENPs integration into nanoproducts					x			x
Release scenarios for ENPs from nanoproducts (product life cycle stage, compartment released to, quantities, “forms”)			x	x	x	x	x	x
Exposure routes		x		x	x		x	
Quality of exposure: Potential uptake paths (lung, skin, ..)	x	x			x			
Behaviour of ENP in technosphere and environmental compartments		x	x	x				
Occupational Health scenarios	x		x	x	x		x	
Consumer Exposure scenarios	x		x	x	x		x	
Dose/ Response-Relationships for ENPs	x	X						
Bioavailability of ENPs	x	X						
Biopersistence of ENPs	x	X	x					
Degradation of ENP in technosphere and environmental compartments under what conditions		X	x					
Relative impact of nanoproducts on human health and the environment	x	x		x				x
Opportunity for material and energy savings or risk for increased material and consumption								x

The scope of Life cycle concepts and risk assessment methods is roughly outlined by showing which relevant information for the development of safe nanoproducts is gained by the application of the different methods or concepts. (Som et al., 2009)

**Risk assessment methods, as well as life cycle methods contribute to exposure studies.*

Appendix 2: CNT review in a LCA perspective. Emphasis on potential releases and exposure to CNT

Article reviewed:

Bauer C., Buchgeister J., Hischier R., Poganietz W. R., Schebek L., Warsen J., 2007, *Towards a framework for life cycle thinking in the assessment of nanotechnology*, Journal of Cleaner Production 16

Summary:

- Generalities about nanotechnologies, in relation to LCA
- 2 cases of studies:
 - Physical vapour deposition (PVD) coating
 - **CNT in electronic sectors: FED screen (field emission display)**
 - ⇒ *CNT as surface coating*

Main conclusions in the context:

- Not a strong focus on human health exposure
- UFP discussed for nanotechnologies in general
- Emphasis on the lack of data, though the two cases were performed (CML method, and Cumulative Energy Demand)
- References to basic materials for CNT (growth of CNT at low temperature; *Hwang et al.*, 2005; energy requirements (electricity) from *Healy et al.* (2006) (20% of the reported value is considered).

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	Materials	Manufacture	Use	Disposal
Energy			<u>Example of the CNT-based FED screen :</u> Domination of energy consumptions at use stage.	
Release potential (Is there any possibility of releases?)	<ul style="list-style-type: none"> - [comment: Use of metals might induce releases, though this is not mentioned at all.] - “Possible” release of ultra-fine particles (UFP; <0.1µm) and their “probable impact on human health”. ⇒ No focus on a particular LC stage 		Release of UFP might arise when using products containing “inherently dispersive nanoparticles” (e.g. personal care products; <i>Reijnders</i> , 2006).	Assumption that releases of CNT out of the vacuum occur, but the point is not covered due to lack of data.
	-	- “Unlikely that releases of nanoparticles occur when vacuum conditions in the coating plant” (case stated for PVD, might also be valid for CNT)	<u>Example of the CNT-based FED screen :</u> CNT layer in the vacuum between two glass layers => no emission assumed	
Exposure (Is there people/living organisms, who could be affected?)			<u>Example of the CNT-based FED screen :</u> [comment: what if the screen breaks ? => release of CNT/UFP to user]	Exposure to waste treatment personals.

Article reviewed:

Khanna V., Bakshi B. R., Lee L. J., 2008, Carbon nanofiber production – Life cycle energy consumption and environmental impact, *Journal of Industrial Ecology* 12(3)

Summary:

⇒ CNF: Surface coating (textiles)

Performing a LCIA of CNF synthesis: “cradle to gate” LCA.

- Major processes are integrated (extraction and manufacture of materials, ending at the synthesis of CNF).
- A material inventory for the manufacture of 1kg of CNF is provided

Main conclusions in the context:

- Not integrating the use and disposal stage
- Not including releases and impacts of CNF on human and ecosystems species during manufacturing (lack of quantifiable data).
- References to *Magrez et al.* (2006), who give evidence of size-dependent hazardous and toxic effects of carbon-based nanomaterials (incl. CNF).

References

Magrez, A., S. Kasas, V. Salicio, N. Pasquier, J.W. Seo, M. Celio, S. Catsicas, B. Schwaller, and L. Forró., 2006, *Cellular toxicity of carbon-based nanomaterials*. *Nano Letters* 6(6): 1121–1125

	Materials	Manufacture	Use	Disposal
Energy	Life cycle energy requirement ranging between 2.8 (with benzene feedstock) and 10.9 GJ/kg (with methane feedstock), which is 13-50 times higher than the requirement for same amount of Al. Mainly due to processes, particularly resources consumed to meet the electrical demand (coal) to maintain high temperatures		Not included	
Release potential <i>(Is there any possibility of releases?)</i>	- Human toxicity mainly due to hydrocarbon feedback (when using vapour-grown carbon nanofibers (VGCNF))			
		- Though releases of CNF are not discussed, it is mentioned that they “can” occur in CNF reactor, in the separation system (separation of CNF and off-gases), in the purification stage (CNF dissolved in solvents), and they are “likely” to occur in processing stages.		
Exposure <i>(Is there people/living organisms, who could be affected?)</i>		[<i>comments</i> : LCA workers]		

Article reviewed:

Khanna V., Bakshi B. R., 2009, *Carbon nanofiber polymer composites: evaluation of life cycle energy use*, *Envir. Science Technol.* 2009, 43, 2078-2084.

Summary:

- Products containing CNT (1st category; e.g. batteries)
 - ⇒ Example of automotive body panels treated (incl. use stage)
- Large emphasis on energy (energetic LCA of PNCs)

Main conclusions in the context:

- Regarding energy, the use stage contribution (relatively to other LC stages) is highly dependent on the type of products
- End-of-life of PNCs not considered, though the likelihood of occurrence of releases and exposure to CNF during the disposal/recycling stage (*The Royal Society*, 2004) is mentioned.

References

The Royal Society, 2004, *Nanoscience and Nanotechnologies: opportunities and uncertainties*. www.nanotec.org.uk/finalReport.htm. Accessed January 2008.

	Materials	Manufacture	Use	Disposal
Energy	Based on a “cradle-to-gate” comparison with steel (with a same functional unit, considering the equal stiffness), PNCs (polymer nanocomposites) induce an energy consumption 1.3-10 times higher (different ranges of CNF ratios and polymer resins were investigated, hence the ranges).		Potential for savings was considered: conclusion was that it is highly dependent on the product itself and its function Example: infrastructure, using CNF will not induce energy requirement, and therefore there is no potential for savings. On the opposite, the substitution of steel by CNF-reinforced PNCs (polymer nanocomposites) in a car would enable savings due to a lighter mass and resulting lower fuel consumptions.	Not included
Release potential <i>(Is there any possibility of releases?)</i>	Not discussed	Not discussed	Not discussed	
Exposure <i>(Is there people/living organisms, who could be affected?)</i>	Not discussed	Not discussed	Not discussed	

Article reviewed:

Healy M. L., Dahlben L. J., Isaacs J. A., 2008, *Environment assessment of single-walled carbon nanotube processes*, Journal of Industrial Ecology 12(3)

Summary:

Assessment of 3 methods of production of SWNT (arc ablation (arc), chemical vapour deposition (CVD), high-pressure carbon monoxide (HiPCO)).

- Production of 1 g of CNT => no distinction according to its use
- Only materials and manufacturing stages (namely processes are catalyst preparation, synthesis of CNT, purification, inspection, packaging)
- Emphasis on electricity in discussions.

Main conclusions in the context:

- Extent of the environmental burden remains uncertain as long as no additional information regarding the environmental and health impacts of CNTs is provided.
- Particularly, more data is needed to enable assessments of impacts of worker exposure during the manufacturing process (“EHS effects of SWNT”) or of SWNT discharges to the environment;

References

Cf. corresponding paper

	Materials	Manufacture	Use	Disposal
Energy	Energy requirements for the three types of production are provided for the two processes: synthesis of CNT and purification of CNT.		Not included	
	Arc	Synthesis 69.73 kWh/g _{CNT-produced}		
		Purification 28.49 kWh/g _{CNT-produced}		
	CVD	Synthesis 230.24 kWh/g _{CNT-produced}		
		Purification 14.77 kWh/g _{CNT-produced}		
	HiPCO	Synthesis 26.49 kWh/g _{CNT-produced}		
	Purification 13.71 kWh/g _{CNT-produced}			
	Note:	High consumptions compared to same production of other materials (e.g. aluminium, wafer Si)		
Release potential (Is there any possibility of releases?)	<ul style="list-style-type: none">- Uncertainties remain as for the environmental impacts which may be associated with dispersion of SWNT into air, water, soil, and the resulting human health effects, via inhalation, ingestion, or dermal contact. [<i>comments: the release potential is not estimated, due to lack of information</i>]- With respect to human toxicity, the impact “Airborne inorganics” was assessed, and it turned out that it had a relatively significant contribution (particularly for CVD). The impact is driven by the electricity production. [<i>comments: No further investigation is performed to be of relevance in the context of our study.</i>]		Regarding energy, the example of a switch, which does not require energy to be used serves to state that the use stage might also be relevant, depending on the specificity of the product.	
Exposure (Is there people/living organisms, who could be affected?)	Workers. Environmental health and safety of SWCNTs is mentioned several times, but cannot be discussed further due to lack of data. On-going works are identified: <ul style="list-style-type: none">- Research is conducted to investigate exposure and effects of CNTs (<i>Hurt et al., 2005; Warheit, 2005; Lam et al., 2006</i>).- Is quoted the on-going research on the capacity of SWCNTs to be inhaled after synthesis without agitation (<i>Baron et al., 2003, Colvin, 2003, Muller et al. 2006</i>)- Proposals for guidelines to ensure public safety and environmental responsibility are under study (<i>Hett 2004; Royal Society & Royal Academy of Engineering 2004; Oberdorster et al. 2005b; Brady et al. 2006; Maynard 2006; Renn and Rocco 2006; EPA 2007; Klöpffer et al. 2007</i>)- In the absence of information, guidelines for best practices in the workplaces have been proposed to limit possible exposure (<i>DOE, 2007; NIOSH, 2007; Ellenbecker et al., 2008</i>)		A very brief example in the field of microelectronics (Central Processing Unit) is given to demonstrate that disposal stage might be relevant if the risk that CNT cause health/environmental effects is proved	

Article reviewed:

Köhler A. R., Som C., Helland A., Gottschalk F., 2007, Studying the potential release of carbon nanotubes throughout the application life cycle, *Journal of Cleaner Production* 16

Summary:

As title suggests, identification of the potential sources of CNT releases through their LC. CNT-oriented approach, meaning that the focus is not on the CNT-containing product itself (battery, textile).

- ⇒ In the perspective of the CNT-containing product, the study then only covers the potential releases from the manufacturing stage (materials are not discussed) till the disposal stage and only related to CNT.

2 cases of study:

- **Li-ion batteries (CNT in a matrix, 1st category)**
- **Textile (2nd category)**

Releases might arise in the forms of :

- Inherently dispersive CNT
- Aggregates of CNT
- Micron-sized composite particles, integrating CNT
- Exposition of free CNT, protruding from the surface of leached matrix material

Main conclusions in the context:

- Identification of potential occurrences of CNT releases and associated risks depending on the different ways of handling the products at different stages (production, use, disposal)
- Correlated exposure briefly discussed, depending on the situation of the releases.
- Impacts on human health and the environment not investigated enough at the moment to conclude on the risks of those potential exposures to CNT. As a conclusion to the study, a precautionary approach is recommended to be implemented, regarding the CNT applications (e.g. use of state of the art exhaust filters).

References

Elsner P. *What textile engineers should know about the human skin*. In: Elsner P, Hatch K, Wigger-Alberti W, editors. *Textiles and the skin*. Basel: Karger; 2003. p. 24-34.

	Materials	Manufacture		Use		Disposal	
		Battery	Textile	Battery	Textile	Battery	Textile
Energy	Not discussed	Not discussed		Not discussed		Not discussed	
Release potential (Is there any possibility of releases?)	<ul style="list-style-type: none"> - Only the synthesis of CNT is considered in this stage. - Gas-phase processes: CNT are formed as an aerosol inside a reactor vessel - If positive pressure => possible leakages - Vapour-phase processes: direct releases unlikely to occur - Recovery phase: CNT may be collected in bag-filters (e.g. gas-phase processes) => risk of releases if inefficient (particularly in case of recirculation of the work place air). Possible re-suspension of CNT into the air when recovery done by automated 	<ul style="list-style-type: none"> - Some substances used are mentioned “moderately toxic and environmentally problematic” (e.g. V2O5, LiCoO2). No discussion about their potential releases is provided. - Potential emissions of CNT in occupational environments might arise at all stages until the cells are sealed (e.g. chemical/physical preparation of the CNT (milling), preparation of the electrodes (e.g. assembling, winding). - Production 	<ul style="list-style-type: none"> - Potential releases at the early stages (when polymers are bleached with nanotubes) - Not considerable releases are expected from experts during spinning and weaving, but might occur at fabric finishing and tailoring (dry and wet abrasion of fibres) 	<ul style="list-style-type: none"> - If properly handled, it is unlikely to have emissions of CNT (due to the sealing/encapsulation) - Release might occur in case of faulty operation (mechanical force, exposure to heat, irregular recharge attempts) 	As CNT are very stable, their potential releases depend on the degradation of the matrix material (potential degradation of polymer due to external influences such as UV-radiation, high T, water, wear and tear, or also internal ageing)	Recycling: CNT-emission scenarios depend on the process details Example: sophisticated technologies might imply shredding, milling and thermal processing, thus generating dust and CNT are likely to be dispersed in air (potential occurrence in exhaust of the recycling facilities, due to filters not designed for nanoparticles. Manual dismantling or primitive technologies “certainly” cause release of CNT and lead to direct exposure in the working environment. Mechanical processing and pyrolysis do not	Recycling: Mechanical, thermal and chemical treatments could possibly result in CNT emissions. If the CNT-containing material is recycled, a cross contamination can be possible (if downcycling to technical products, CNT become no longer traceable) Incineration In proper installations, one “can assume that the CNT/polymer composites incinerate completely”. In case of surviving CNT enter the waste gas stream, they will form agglomerates with dust particles and deposit in waste

	<p>or manual removal from the deposition substrates (vapour-phase processes).</p> <ul style="list-style-type: none"> - Likelihood that during recovery, and further processing (handling, packaging), CNT are released as agglomerated bulk powder rather than individual CNT. - Possible releases when cleaning and maintaining the installations as well as at the disposal of materials (e.g. dust collection system). 	<p>waste and contaminated facilities and supplies (e.g. inert gas) might be a source of CNT releases.</p> <ul style="list-style-type: none"> - Overall, likelihood of releases depends on types of facilities, safety installations, operational concept and process design. 				<p>eliminate CNT (“transferred into granulate interstage products”), which become then large potential sources of releases, because the handling operations take place outside controlled environments.</p> <p>Incineration:</p> <p>Usually ignition of CNT in presence of O₂. In case of densely packed CNT, it might survive the incineration. Cylindrical cells might still then contain CNT when entering the slag (<i>comment: potential releases in landfill ?</i>).</p> <p>Landfill:</p> <p>Risk of leakages due to battery corrosion. Migration to air as dust, or soil or flushed away by water</p>	<p>gas filter [<i>comment => no releases</i>]</p> <p>In case of uncontrolled incineration in open fires (developing countries), CNT might not be destroyed and might enter the ashes or the fume.</p>
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Exposure <i>(Is there people/living organisms, who could be affected?)</i>	- Workers at the production plant (incl. maintenance people).		Users	Dermal exposure to CNT might induce health effects such as skin irritation <i>(Elsner, 2003)</i>	Workers in waste treatment facilities (case for recycling with manual dismantling); <u>[comments: People living in the surroundings of the recycling facility]</u> <u>[comments: All living organisms next to the landfill area.]</u>
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Article reviewed:

Kushnir D., Sandén B. A., 2008, Energy requirements of carbon nanoparticles production, Journal of Industrial Ecology 12(3)

Summary:

- Provide energy requirements for production of CNP
 - ⇒ For several methods used (e.g. CVD)
 - ⇒ Influence of critical factors on the energy demand identified
- Energy requirements, with a ‘cradle to gate’ perspective

Main conclusions in the context:

- Provide figures for energy requirements for different methods and for different processes
- No mention of other issues (potential releases and exposure of/to CNT)

References

	Materials	Manufacture	Use	Disposal
Energy	Energy requirements provided for 1 kg of CNP produced (Carbon nanoparticles) for different processes: <ul style="list-style-type: none"> - Net feedstock - Catalyst bed production - Acid production - Gas purification - Process heating - Compression - Purification processes For both thermal and electricity and for different methods of production		Not discussed	Not included
Release potential <i>(Is there any possibility of releases?)</i>	Not discussed	Not discussed		
Exposure <i>(Is there people/living organisms, who could be affected?)</i>	Not discussed	Not discussed		

Article reviewed:

Seager T. P., Raffaele R. P., Landi B. J., 2008, *Sources of variability and uncertainty in LCA of single wall carbon nanotubes for Li-ion batteries in electric vehicles*. Proceedings from IEEE international symposium on electronics and the environment

Summary:

- Overall, difficulties to perform LCA due to the large variability in nanomaterials and in their ways of production; uncertainties in the toxicology and risks of nanomaterials, and a lack of data concerning their end-of-life.
- Discussion illustrated with case of a SWCNT-based Li-ion battery for use in automotive applications.
- An example of functional unit relevant to the use phase was defined as “miles driven” for the case of study.
- Difficulty to characterize toxicity and environmental risks as for SWCNT (surface properties, interaction with environmental media or microbial activation not possible to capture in terms of mass concentrations). No existing LCA midpoints may be meaningful.

Main conclusions in the context:

- Not much relevant in the goals of this review

References

	Materials	Manufacture	Use	Disposal
Energy	Not discussed	Large dependence on the method used to produce the SWCNT and the properties of the SWCNT, which are required	Not discussed	Not included
Release potential <i>(Is there any possibility of releases?)</i>		Not discussed		
Exposure <i>(Is there people/living organisms, who could be affected?)</i>		Not discussed		

Article reviewed:

Olapiriyakul S., Caudill R. J., 2008, A framework for risk management and end-of-life (EOL) analysis for nanotechnology products: a case study of Li-ion batteries. Proceedings from IEEE international symposium on electronics and the environment

Summary:

⇒ Products containing CNT: batteries (1st case)

- **Emphasis on end-of-life of the battery and its recycling.**
- Not particularly strong focus on CNT, even though they are discussed separately along with nanoparticles in general.
- Contain a unit process diagram for the pyrometallurgical recovery process, with identifications of possible nanoparticles releases

Main conclusions in the context:

- Potential releases through the filtration system (after wet scrubber), if not adapted, and through slag/unmelted materials, in case the CNT is preserved from oxygen during the reduction process.
- Occupational exposure at recycling facilities [*and workers/users in contact with recovered products/materials; AL comments*]

References

	Materials	Manufacture	Use	Disposal
Energy	Not discussed	Not discussed	Not discussed	<p>Necessary increase of the energy consumption (at the smelting stage) in order to overcome the problem of melting point elevation (in to the reduction process, where CNT might remain if not oxidized).</p> <p>Subsequently to this, the example of a current process calculated to consume 2.916 GJ per ton of finished material, which would have to be raised to 3.6 GJ/ton.</p>
Release potential <i>(Is there any possibility of releases?)</i>				<ul style="list-style-type: none"> - During the EOL recycling operations (e.g. shredding process), potential generation and releases of small nanoparticles through conventional filtration system might occur (small nanoparticles may follow the Brownian motion and therefore get through the filter) - CNT encapsulated in a non-oxide host matrix, with a melting point higher than the reduction temperature, may survive the reduction process (because not exposed to oxygen), and therefore remain with the unmelted materials (e.g. Contamination of the recovered metals and slag by unmelted nanomaterials)
Exposure <i>(Is there people/living organisms, who could be affected?)</i>				<ul style="list-style-type: none"> - Occupational exposure in case of insufficient filtration system. - [<i>comments: Exposure to workers and users in contact with the recovered metals (affected by contamination)</i>]

Article reviewed:

Sengül H., Theis T. L., Ghosh S., 2008, Toward sustainable nanoproducts – An overview of nanomanufacturing methods. *Journal of Industrial Ecology* 12(3)

Summary:

- Thorough review of manufacturing techniques of nanomaterials
- Environmental impacts not deeply detailed

Main conclusions in the context:

- No focus on CNTs
- Mainly manufacturing techniques developed, with a brief mention of chemical exposure
 - ⇒ Not much relevant for the review

References

Petkewich, R. 2007. *Nanotube synthesis emits toxic by-products*. ACS Meeting News. <http://pubs.acs.org/cen/news/85/i35/8535news9.html>. Accessed August 2007.

	Materials	Manufacture	Use	Disposal
Energy	Not discussed	Not discussed	Not discussed	Not discussed
Release potential (Is there any possibility of releases?)		<ul style="list-style-type: none"> - “PAHs (pyrene and xylene) are used as precursors for the growth of CNTs”. Mention of a source identifying emissions of 15 aromatic hydrocarbons, including 4 different kinds of toxic PAHs, occurring in the synthesis of nanotubes (Petkewich, 2007). - Potential releases of CNTs as agglomerated powder from bag filters [<i>comment: already mentioned in the review of Kohler et al., 2008</i>] 		
Exposure (Is there people/living organisms, who could be affected?)		[<i>comment: Workers</i>]		

Article reviewed:

Claudia Som, Marcel Halbeisen, Andreas Köhler, 2009b: Integration von Nanopartikeln in Textilien, Abschätzungen zur Stabilität entlang des textilen Lebenszyklus. Report from EMPA www.empa.ch/nanosafetextiles

Summary:

Report from Nanosafe textiles project sponsored by TVS Textilverband Schweiz and the Empa.

- Thorough review of techniques for incorporation of nanomaterials in textiles and the stability of the integration of nanoparticles
- Environmental impacts not deeply detailed

Main conclusions in the context:

- There are no unequivocal evidence of potential for release but fairly sound estimates have been produced based on the theoretical knowledge of how nanotextiles are produced and used
- Nanoparticles (NP) can be integrated in quite different ways into textiles: into the fiber, on the surface of the fibers or in the textile matrix.
- The NP can be bound more or less strongly depending e.g. on type of chemicals, type of textile , functionalisation of the NP, process technical parameters in the manufacturing, further process steps of the textile after the binding.
- The release depends on the binding of NP and on influences on the textiles during its life cycle, e.g. mechanical stress, washing, UV-light, solvents etc.
- The NP can be released as single NPs, agglomerated NPs or nano- or micro meter scale textile containing NP.

	Materials	Manufacture	Use	Disposal
Energy	Not discussed	Not discussed	Not discussed	Not discussed
Release potential <i>(Is there any possibility of releases?)</i>	Not discussed	Not discussed	Depends very much on the type of NP, the textile and the way NP and incorporated	Not discussed
Exposure <i>(Is there people/living organisms, who could be affected?)</i>	Not discussed	Not discussed	Not discussed	Not discussed

Appendix-3: Calculation of potential exposure to Carbon Nanotubes from the release of CNT from clothing made from textiles fibres coated with CNT

As discussed in Section 3.4.2, CNTs have properties that may have great advantages for textiles and clothes. With a reduction in the production costs, CNTs may become widely used in fabric and textiles in the future. It is therefore important in relation to consumer safety to estimate how much CNT could be released through wear and tear during use stage of the CNT-containing textiles and cloths, and how much inhalation exposure of the consumer to CNT could take place.

- CNT may be present as fibre bundles but it may be likely that wear and tear would cause release of “single” fibres, rather than as obvious visible large threads.
- For illustration, it is informative to consider the scenario that CNT might be released as single “fibres” with a length of 15000 nm. (Note that this is a length that would cause concern for health effects, as it is the minimum length referred to by Poland et al, 2008 as being pathogenic). If the diameter of each CNT is 100 nm, and taking the density of graphite as 2.25 g cm^{-3} , then the mass of one such CNT would be $2.65 \times 10^{-16} \text{ kg}$.
- If the concentration in air of CNT of the above size is 1 fibre per cm^{-3} , then the mass concentration of CNT would be $2.65 \times 10^{-7} \text{ kg m}^{-3}$. In terms of mass concentration, that would be very difficult to measure by any gravimetric method.
- The sedimentation rate of CNT of the above dimension would be extremely low, due to the fibre having a very low gravitational settling velocity. The release of CNT from CNT-fabrics could lead to a cumulatively increasing concentration in public buildings or other enclosed spaces.
- The concentrations that might arise from release of CNT from clothing will vary in different circumstances, in particular the amount of dilution. Circumstances will range from the outdoors to a crowded indoor situation, such as busy shop, rush hour in buses or trains, and the crowded disco or packed school assembly hall. The amount of ventilation within each situation may also vary, and the extent of activity that could cause fibre release is also likely to vary (e.g. high levels of movement and contact in discos and busy public transport).
- The rate at which CNT may be released is unknown, but it is perhaps useful to ask if a rate of release that would be equivalent to generating 1 fibre per cm^{-3} into an immediate near volume of 2 m^3 of air would be a noticeable loss of fabric. The commuter in a crowded train standing shoulder to shoulder with other commuters will have much less space.
- On the basis of the above calculation of the equivalent of mass and fibre number, the amount of material loss that might suffice to generate 1 fibre per cm^{-3} in 2 m^3 of air would be $2 \times 2.65 \times 10^{-7} \text{ kg} = 5.3 \times 10^{-7} \text{ kg} = 0.53 \text{ mg}$. If it were a lightweight garment such as a T-Shirt, weighing about 250 g (of which around 10% = 25 g might be the CNT), the loss of 0.5 mg in 25000 mg would not be noticeable for a wearer of a garment.

From the above estimates, and subject to the rate of release of CNT, if such CNT-coated-fabric garments are worn by majority of the persons in a crowded space, the concentration of airborne CNT could become significantly elevated. The uncertainty in this regard is that the actual rates of release of CNT from different types of CNT-containing textiles and clothing are unknown and therefore need to be experimentally determined to confirm the estimated releases.